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Influence of polymeric additives on the melting and crystallization behavior of nylon 6,6.

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INFLUENCE OF POLYMERIC ADDITIVES ON THE MELTING AND CRYSTALLIZATION BEHAVIOR OF NYLON 6,6

A DISSERTATION

Submitted to the College of Engineering and Mineral Resources
of
the West Virginia University

In partial fulfillment of the requirements for
the Degree of
Doctor of Philosophy
in
Chemical Engineering

By
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Morgantown, WV 26506, USA
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Dedicated
to
my parents Mohinder and Shanti Walia

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ABSTRACT

The goal of this research was to find polymeric additives that would influence the amount of spherulitic growth in nylon 6,6. In particular, it was desired to decrease the rate of crystallization by a significant amount in order to enhance mechanical properties indirectly. While there are several ways in which this growth reduction could be achieved, the technique considered the most promising was the introduction of miscible polymeric additives. For commercial applications, keeping the additive concentration below 10% by weight is generally desirable. The search for such miscible polymer additives constituted the first half of this project.

Since miscibility was essential, different classes of materials considered included amorphous nylons, semi-crystalline nylons and other polymers known to be compatible with polyamides. These additives were blended with nylon 6,6 using solution and melt blending techniques developed as part of this research. The change in thermal behavior of the blends was evaluated using data obtained with a Differential Scanning Calorimeter (DSC) and Dynamic Mechanical Thermal Analyzer (later part of the work). Reduction in the crystallization temperature (T_c) during a non-isothermal DSC run was used as the primary criterion for judging the effectiveness of the additive.

Polymers that were particularly promising included amorphous nylons - Trogamid-T and Zytel 330; nylon 6,12 and polyacrylic acid. An unusual finding was that annealing the blend in the melt state promoted additional changes in the melting and crystallization behavior. This was attributed to interchange reactions occurring between the blend components. Based on such considerations as ease of processing, availability and cost, later work was focussed on the use of nylon additives. In this regard, understanding the mechanism of additive action was necessary, including the influence of the nature of additive, amount of additive, residence time in the extruder, drying time, and the time of annealing in the melt. Experiments were conducted to better understand the effect of these reactions on the thermal behavior and constituted the second phase of this project.

Both the amorphous and semi-crystalline additives produced significant changes in the thermal behavior as a function of melt annealing, the effect increasing with concentration. It was found that Trogamid-T was more effective in reducing the rate and extent of crystallization of nylon 6,6 when compared with nylon 6,12, as revealed by the non-isothermal and isothermal DSC runs. The suppression in T_c was more for the as-prepared Trogamid-T blends and also for samples annealed for different times. The extent of interchange reaction, measured by the depression in equilibrium melting point, was linear with respect to the annealing time. Trogamid-T blends appeared to be "nearly miscible" initially, with miscible blends being produced in the twin screw extruder at all concentrations. The T_g-composition curve showed a positive deviation from linear additivity. The single T_g decreased as a function of annealing time in the melt, with the change in T_g being proportional to the additive concentration.

This work clearly established the effect of interchange reactions on the thermal properties of nylons. The effect of the above-mentioned variables on these reactions was understood. The importance of the level of mixing on the extent of reaction was shown and a method of improving miscibility using these reactions was demonstrated.

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CHAPTER 1

INTRODUCTION & OBJECTIVES

1.1 Crystallization in Polymers

Referring to crystallinity in polymers may seem strange since polymers are only long, randomly coiled chains of molecules, with relatively weak intermolecular or secondary bonds. In metals, true crystals form because of strong ionic or metallic bonds. In polymers also, crystal structures form because of arrangements of chains into close-packed, ordered structures. However, the difference between metals and polymers lies in that the metallic crystals form readily throughout the material. In bulk polymers, crystallization does not extend throughout the domain because of the long chain nature of molecules and irregularities, such as side branches and entanglements; therefore polymers can be semi-crystalline, at best. The non-crystalline part is amorphous, i.e., consists entirely of randomly arranged chains. Also, not all polymers can form close-packed, ordered supramolecular structures called crystallites or spherulites; only molecules that have regular, periodic location of chemically packed monomers, associated with high secondary bonding forces, are crystallizable.

The molecules fold back and forth with hairpin turns in crystalline polymers. These folded chains are organized into thin, plate-like lamellae (Figure 1.1, taken from ref. 1). Single lamellae are observed only on precipitation from extremely dilute polymer solutions. In a polymer crystallized from the melt, the lamellae are separated, and the spaces between the lamellae are filled with amorphous or randomly arranged molecules. The function of the

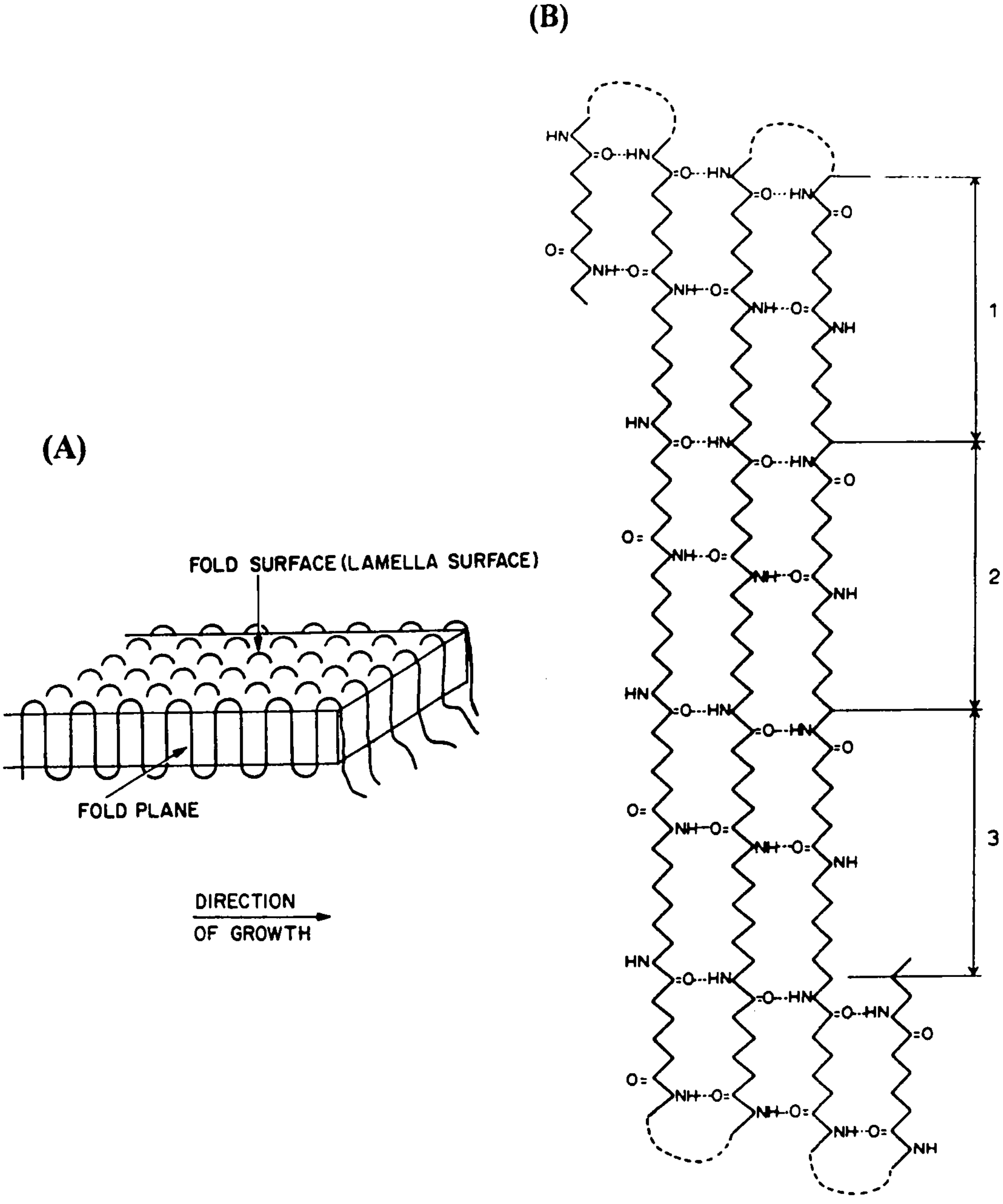


Figure 1.1: Crystalline structure of nylon 6,6 (from ref. 1) :
(A) Organization of chains into lamallea
(B) Triclinic unit cell

amorphous material is to tie all the lamellae together. In polymers of sufficiently high crystallinity, the lamellae aggregate spontaneously and organize into larger structures of distinctive appearance known as *spherulites*. The unique feature of these spherulites is the appearance of Maltese Cross patterns in an optical microscope under crossed polarizers (Figure 1.2 [2]). Spherulites range in size from submicroscopic (below 1 μm) to about 50 μm in commercial polymers. The thickness of the folded-chain lamellae within the spherulites is from 10 to 100 nm or of the order of 100 atoms.

Each spherulite grows radially from a nucleus formed either homogeneously or by the presence of an impurity in the system (heterogeneously). Usually the spherulites are spherical in shape only during the initial stages of crystallization. During the latter stages, the spherulites impinge on their neighbors (Figure 1.2B). Since spherulites are nucleated at different times, they are different in size when they impinge on one another, and therefore their boundaries form hyperbolas.

The rate of crystallization is strongly dependent on temperature. Crystallization is bounded between the glass transition temperature (T_g) and the melting temperature (T_m). Below T_g, the chains are essentially frozen and are not free to move about and therefore cannot arrange into any crystalline shape. Above T_m, the chains acquire enough energy to break the ordered structure. At temperatures between T_g and T_m, two main factors influence the rate of crystallization: (i) the rate of nucleation; and (ii) the subsequent rate of growth of these nuclei to spherulites. Crystallization or spherulitic growth rate reflects the competition between the nucleation rate and the rate of transport or diffusion in the melt. A typical rate of crystallization versus temperature plot is shown in Figure 1.3. When the temperature is

Figure 1.2: A thin section of bulk crystallized nylon, in polarized light, reveals a bright, birefringent and spherulitic texture. In the overview (A) the spherulites range from nearly round to polygonal in shape. At higher magnifications (B,C) a classic Maltese Cross pattern is seen, with black crossed arms aligned in the direction of the crossed polarizers [from ref. 2]

close to T_m, the nucleation rate is slow and hence only a few large spherulites are formed. Rates of transport in the melt decrease with temperature and these low rates dominate near T_g. However, at lower temperatures, nucleation is faster and several small spherulites are formed. Between T_g and T_m, the crystallization rate passes through a maximum, as illustrated in Figure 1.3. The number, size and perfection of spherulites formed is strongly dependent on the thermal history that the polymer experiences.

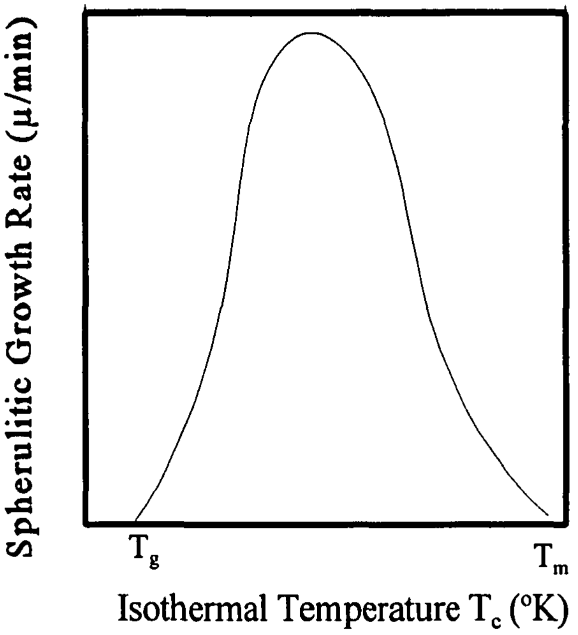
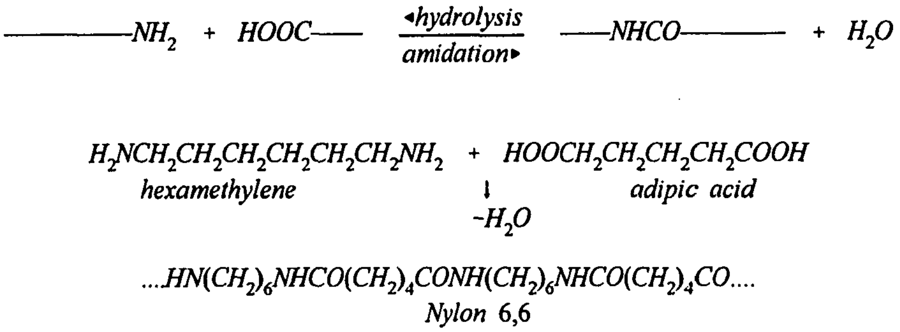


Figure 1.3: A typical rate of crystallization versus temperature plot for a semi-crystalline polymer

1.2 Properties of Nylon 6,6

Nylon 6,6 is a linear polyamide, the condensation product of the reaction between adipic acid and hexamethylene diamine (Figure 1.4); typical molecular weights range from 15,000 to 25,000. A characteristic feature of this polymer is the ability of the amide linkages to hydrogen bond with each other. This, coupled with a regular structure, results in a highly crystalline material having as much as 40-50% crystallinity by weight. It is found [1] that nylon 6,6 crystallizes into folded chain lamellae with amide linkages at the folds. The unit cell is triclinic containing only one chemical repeat unit with adjacent hydrogen bonded sheets displaced parallel to one another by the equivalent of three chain atoms to accommodate the packing of the amide groups (Figure 1.1). When crystallized from the melt, especially upon slow cooling, nylon 6,6 forms spherulites.



$$—NH_2 + HOOC— \underset{amidation\blacktriangleright}{\overset{\blacktriangleleft hydrolysis}{\rule{2cm}{0.4pt}}} —NHCO— + H_2O$$

$$\underset{hexamethylene}{H_2NCH_2CH_2CH_2CH_2CH_2CH_2NH_2} + \underset{adipic\ acid}{HOOCH_2CH_2CH_2CH_2COOH}$$

$$\downarrow -H_2O$$

$$\underset{Nylon\ 6,6}{\ldots HN(CH_2)_6NHCO(CH_2)_4CONH(CH_2)_6NHCO(CH_2)_4CO\ldots}$$

Figure 1.4: Chemical Structure of Nylon 6,6

The highly crystalline nature of nylons governs many of their important physical and mechanical properties. The crystallinity present has a significant influence on most of the mechanical properties (Table 1.1 [ref 1]). The melting point of nylon 6,6 is about 260°C and it increases with increasing molecular weight. The reported [3] heat of fusion value for nylon

6,6 is 188.1 J/g (45 cal/g) for the 100% crystalline material. Usually, the higher the amide concentration in a polyamide, the higher is the melting point. Mechanical properties, such as elastic modulus, yield strength, hardness, and abrasion resistance, typically increase with increasing extent of crystallinity. Measures of toughness, such as impact strength, decrease, particularly in the high crystallinity range. The size and morphology of spherulites also have a direct influence on the physical properties. The mechanical properties can hence be altered by changing the nature and amount of crystallinity.

TABLE 1.1: EFFECT OF INCREASING CRYSTALLINITY ON PROPERTIES OF NYLONS

PROPERTIES RISE	PROPERTIES DROP
Stiffness or Modulus	Impact Resistance
Density	Elongation
Yield Stress	Thermal Expansion
Chemical Resistance	Permeability
Electrical Properties	Swelling
T_g and T_m	Mechanical Damping
Abrasion Resistance	
Creep Resistance	
Dimensional Stability	

A major concern during the processing of nylon 6,6 is water absorption. Although the amount of water absorbed decreases with increasing crystallinity, equilibrium values can reach 10% by weight at room temperature and 100% relative humidity. Since nylons are condensation polymers (as shown in Figure 1.4), the degree of polymerization (or molecular weight) is influenced by the amount of water present. While the nylon resin is unaffected by room temperature moisture, the presence of water in the molten polymer can lead to hydrolysis and a reduction in molecular weight. Conversely, there can be post condensation and increase in molecular weight if the polymer being processed is extremely dry. Separately, but importantly, nylon 6,6 can also undergo thermal and shear degradation during processing.

The rate of crystallization of nylons depends [1] on the amide concentration and molecular symmetry, increasing with increasing values of both these quantities. Thus nylon 6,12 and nylon 6,10 crystallize at a lower rate than nylon 6,6. Disruption of the regular molecular structure is a known method for decreasing the rate of crystallization. The presence of moisture enhances the rate of crystallization further, by decreasing the T_g [4,5]. For a non-isothermally cooled polymer, though, the observed crystallinity will depend not only on the intrinsic crystallization rate but also on the time spent at temperatures between T_m and T_g. Note that the glass transition temperature is significantly influenced by the moisture content and can range from 45°C to 85°C. Water acts as a plasticizer and lowers the T_g. Also, water influences the physical properties directly as well as indirectly by affecting crystallinity.

1.3 Research Objectives

From the previous discussion it would have become apparent that the mechanical properties of nylons are closely linked with the amount, size and perfection of spherulites present. Crystallization in nylons is very rapid as compared with other polymers and complete crystallization takes place in most polymer processing operations. By reducing the rate of crystallization the mechanical properties can be controlled indirectly.

The basic objective of this work was to identify polymeric additives that would significantly reduce the rate of crystallization of nylon 6,6. The effect of polymeric additives on the crystallization process of nylon 6,6 was to be examined and understood. The effect of the type and the concentration of the additive was to be investigated. It was desired that the additive should not deteriorate any physical properties of nylon 6,6.

In a given polymer processing operation, a reduction in the observed degree of crystallization can be achieved by (I) reducing the crystal growth rate, (ii) reducing the time available for growth, and (iii) reducing the equilibrium degree of crystallization. The basic strategy adopted in this work was to blend various nylons with nylon 6,6, since the similar chemical structure would give relatively miscible melts or solutions. The highly hydrogen bonded, crystalline nature of nylon 6,6 makes it virtually impossible to find [6] miscible macromolecular additives and this was one of the challenges to be overcome in this work. However, several low molecular weight solvents such as phenols, formic acid and mineral acids do exist. However, environmental concerns preclude their use. The rest of the dissertation describes the strategy used in the selection of the additives, the results obtained with the selected additives and the interpretation of these results.

CHAPTER 2

METHOD OF APPROACH

There were broadly two stages to the project:

(1) Initial evaluation of a large number of additives prepared by solution/melt blending with emphasis on ease of preparation: The melt blending in this portion of the work was carried out on the Maxwell extruder. Also at this stage, the additive amount was not held below 10% by weight, since larger effects would be expected with the higher additive amounts. The evaluation was based primarily on the DSC data (non-isothermal and isothermal runs). The reasoning used in the selection of the additives and the results from these blends are presented later in Chapter 6.

(2) Selection of a limited number of promising additives for detailed study: This included data from DSC, DMTA, intrinsic viscosity, optical microscopy and RMS-800 rheometer. In this stage, experiments were conducted with controlled moisture content, molecular weight and degradation. The objective was to gain an insight into the mechanism of interaction and the effect of the interaction on the crystallization behavior. Trogamid-T (amorphous) and nylon 6,12 (semi-crystalline) were selected based on preliminary evaluation. Variables examined in the detailed experimentation stage were:

(I) *Molecular weight changes during extrusion (extent of drying):* Since moisture is a critical factor in nylon processing, proper drying conditions needed to be fixed. The drying conditions used were 110°C and 0.2-0.4 mm Hg absolute pressure. If moisture is lower than the equilibrium value then the molecular weight will increase on extrusion (postcondensation) and vice versa. The drying times that would lead to postcondensation and constant molecular weight were determined. This was carried out by comparing intrinsic viscosity (IV) measurements of the unextruded polymer (dried for different times) with that of the extruded one. An increase in IV signifies an increase in molecular weight and vice versa. For a wet polymer, molecular weight can decrease on extrusion. Two drying times were selected, corresponding to the two conditions mentioned above.

(II) *Mixing time in the extruder:* This was investigated with two values: 5 and 30 min. The higher residence time in the extruder was achieved by blocking the end of the die with a plug. This would reveal the effect of shearing, and hence improved mixing, on the blending process and would be relevant for immiscible blends or blends close to miscibility. Better mixing will create more interfacial area and hence speed up the interchange reactions, leading to faster phase homogenization. By comparing data from 30 min residence time samples with those simply annealed in the DSC for 30 min, differences in thermal behavior could be detected.

(III) *Blend composition:* For the most part, two concentration levels were selected: 10 and 5% wt/wt additive amount to see the level of interaction and hence the change in thermal properties achieved at the lower additive concentrations.

(IV) *Additive type:* Amorphous vs. semi-crystalline, to see any differences in the type of interaction.

Hence four variables, at two levels, were evaluated. This gives a total of 2^4 or 16 blends to be prepared to encompass the different variables.

The following experiments were conducted on these blends.

(i) DSC: Non-isothermal (to measure T_c) and isothermal runs (to measure actual crystallization times). In addition, the chemical reaction between the blend components was followed indirectly through the equilibrium melting point depression, by means of the Hoffman-Weeks plot.

(ii) DMTA: Measurement of T_g of the as-prepared sample and samples annealed for different times. This would reveal the initial miscibility of the components and the change in miscibility as a function of any interchange reaction.

(iii) Intrinsic Viscosity (IV): The IV of the extruded blend sample was compared with that of unextruded material. Since the IV values are directly related to molecular weight, the effect of reaction on molecular weight could possibly be seen through such measurements.

(iv) Optical Microscopy: For studying actual spherulitic crystal growth and the effect of the additive on this growth.

(v) RMS-800: To study miscibility of the blend in the melt phase as well as the influence of the interchange reactions on the rheology of the system.

CHAPTER 3

LITERATURE REVIEW

3.1 Blends

The pronounced interest in polymer blends during the past decade is reflected in the large number of papers published in this research area. This interest is not only academic, as polymer blends are also very attractive for industrial applications. Mixing polymers to produce blends and alloys is an important method of achieving desired physical, economic or processing properties, thereby eliminating the need to synthesize new polymer systems. Thus, commercially useful materials can be developed by simply melt blending already existing polymers. The list of such commercially available blends is enormous [7-10].

Before discussing how the additive may influence the blend properties, a distinction between compatible and incompatible blends needs to be made, since compatibility allows for the possibility of combining good properties of the components. It is generally true that, unless partially compatibilized, blends of thermodynamically immiscible polymers exhibit poor mechanical properties due to the lack of interfacial adhesion. In addition, the high interfacial tension between the polymers in the melt can lead to an unstable morphology even under good mixing conditions. This is primarily due to the poor dispersibility and the coalescing tendency of the phases. Thermodynamic compatibility refers to miscibility at the molecular scale. For this to occur, the Gibbs free energy of mixing, ΔG_m, has to be negative:

$$\Delta G_m = \Delta H_m - T\Delta S_m \qquad \ldots(1)$$

Since the entropy of mixing, ΔS_m, is very small, this is only possible if the enthalpy of mixing,

ΔH_m, is negative. That only occurs in limited cases, where the cohesive energy density is closely matched or if the components have specific polar interactions.

Compatible blends can also be defined as mixtures that do not exhibit gross symptoms of phase separation. This would then include several blends compatibilized by the addition of a third component or by reactive extrusion [10]. An excellent review of such available compatibilizers has been given by Xanthos [11]. The effect of compatibilizers is to reduce the interfacial tension in the melt, leading to a finer dispersion of one phase in the other. It also increases the adhesion at the phase boundaries giving improved stress transfer. Reactive extrusion is a popular method of compatibilization in which two polymers containing mutually reactive functional groups are melt blended leading to the in-situ formation of the desired block or graft copolymer. This differs from other compatibilization methods in that the addition of a third component is not needed. The blend components are chosen or altered so that the reaction occurs during melt blending. Reactive blending has been commercially used, for example, in blends of polycarbonate and polyesters, and toughened polyamides, which are blends of polyamides with graft-functionalized polyolefin elastomers. A number of reactive blending mechanisms may be used [10]:

1. Formation of graft or block copolymers by chemical bonding between reactive groups on component polymers. This may be induced, for example, by the addition of a free radical during blending.
2. Formation of a block copolymer by an interchange reaction in the backbone bonds of the components. This is most likely in condensation polymers.
3. Mechanical scission and recombination of component polymers to form graft or block

copolymers. This is generally induced by high shear rates during processing.

4. Promotion of reaction by catalysis.

The use of block or graft copolymers is the most widely used approach in the compatibilization of blends. Block copolymers contain blocks chemically identical to the blend components and miscibility between the copolymer segments and the corresponding blend component is assured. The copolymer locates preferentially at the blend interfaces and the classical view of this type of preferential location is represented in Figure 3.1 [10]. Experimental verification that this happens has been found in many systems [10].

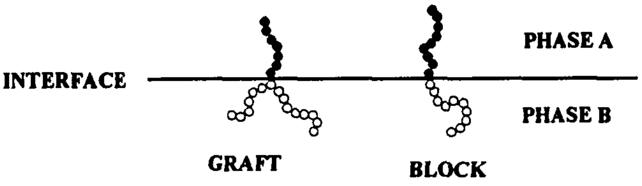


FIGURE 3.1 Schematic representation of block and graft copolymers at phase interfaces

3.2 Thermal Behavior of Blends

The following discussion includes blends of a semi-crystalline polymer with an amorphous polymer and another semi-crystalline polymer. The thermal behavior and the overall morphology of crystallizable binary blends are strongly dependent on factors such as the composition, molecular mass and crystallization conditions. Quantities such as nucleation density, radial growth rate of spherulites, overall rate of crystallization and equilibrium melting temperature, are all influenced by these factors. The type of dependence is related to the physical state of the melt, which at the crystallization temperature, T_c, is in equilibrium or in coexistence with the solid phase that is developing. The blends can be divided into two main groups, based on the physical state of the melt:

1) If the components are compatible at all T_c, then a one-phase melt system results. A non-crystallizable component will act as a diluent and the following effects [11,12] are observed:

I) Depression of the observed and equilibrium T_m with a linear dependence of ΔT_m on the square of the volume fraction of the non-crystallizable component.

ii) Depression of the radial growth rate of the spherulites when T_g of the additive is more than the T_g of the crystallizable component [13]. The miscible blend T_g in this case is higher than that of the crystallizable component. As in pure components, the crystallization in miscible blends is restricted to temperatures between T_g and the equilibrium T_m. Crystallization rates reflect the competition between nucleation rate and the rate of transport or diffusion in the melt. Therefore the (T_g-T_m) range is suppressed. This is illustrated in Figure 3.2. A higher blend T_g signifies lower chain mobility at a given temperature and slower diffusion rates. This results in lower spherulitic growth rates. On the other hand, if the T_g of the additive is lower than the T_g of the crystallizable polymer, the blend T_g is lower. An increase (Figure 3.2) in (T_g-T_m) range is observed in this case. Hence, crystallization rates will increase.

iii) For a blend of the above type, it is found that the non-crystallizable component is trapped in interlamellar regions where a homogeneous amorphous phase is likely formed. Due to this, the distance between adjacent lamellas is found to increase with the content of the non-

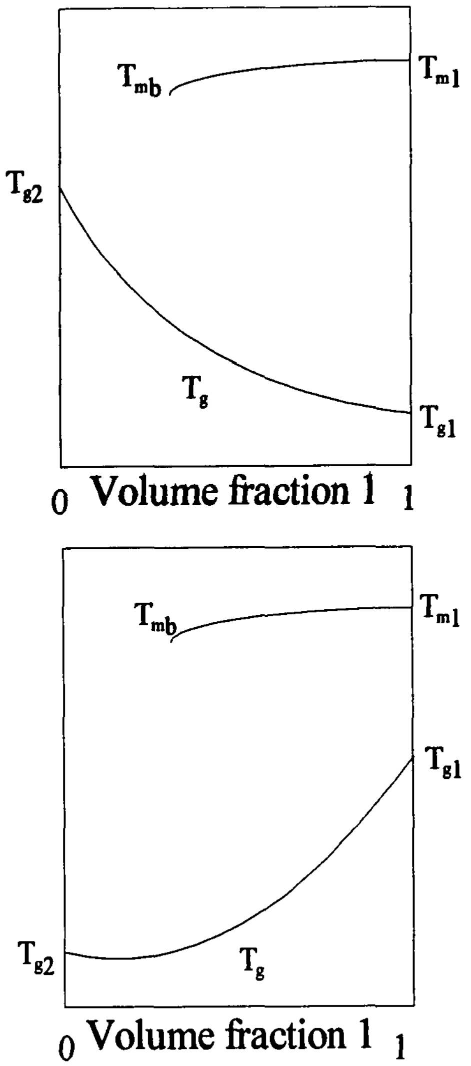


Figure 3.2: Effect of miscible amorphous additive on the T_g and T_m of the blend (semi-crystalline polymer 1 and amorphous polymer 0)

crystallizable component.

iv) The degree of crystallinity is not expected to change for the above type of blends [13]. If the crystallization is carried out at temperatures not approaching the blend T_g, the crystalline components should develop, given sufficient time, a level of crystallinity similar to the pure state.

Hence, both the rate of crystallization and the morphology of the crystallizable component can be altered by this method. The above strategy has been adopted by many workers [13-15]. In compatible blends of semicrystalline PEEK (poly ether ether ketone) and amorphous PEI (poly ether imide), it was found that these polymers were completely miscible in the melt over the entire composition range. The blends exhibited a single T_g at all concentrations, confirming miscibility [14,15]. The rate of crystallization of PEEK was significantly lowered by the addition of PEI. In fact, while pure PEEK could not be injection molded to give an amorphous sample, this was easily accomplished by blends containing 25% or more PEI. Clearly, the magnitude of the effect increases with increasing additive concentration. It also depends on the chemical nature of the modifier and its molecular weight.

2) When the two polymers are incompatible in the melt, the crystallizable component will grow in equilibrium within its own melt phase, with the non-crystallizable component dispersed in the melt as droplet-like domains (e.g., nylon/rubber blends). Depression of the radial growth rate can still be observed because these domains may be rejected, occluded or deformed by the growing spherulites [16,17]. The presence of domains in the form of small or large droplets in the path of the crystallizing front can affect the spherulitic growth. A

depression of the observed and equilibrium melting point, caused mainly by kinetic and morphological factors, is also often observed. This effect, however, may depend in some complex way on the temperature and composition. Also, the addition of the second component may induce the process of heterogeneous nucleation, therefore affecting the overall crystallization rate. In addition, variations in some morphological and structural quantities such as shape, dimensions and distribution of spherulites and interspherulitic boundary regions, and lamellae and interlamellar thickness, are observed. In some cases the formation of new boundary lines connecting the occluded particles is also seen [16,17]. Nadkarni et al. [18] observed this behavior with blends of semi-crystalline polymers polyethylene terephthalate (PET) and polymethyl methacrylate (PMMA), where PET crystallization was enhanced in the presence of PMMA phase. It was postulated that faster nucleation process was induced by the presence of long PMMA molecules in the molten state. There was a higher chance of getting strained PET chain segments in the blends due to the restriction caused by the PMMA molecules on the mobility of PET. The strained chain segments then act as homogeneous nuclei.

In the above discussion, non-crystallizable component refers to an amorphous polymer. The effect of blending two semi-crystalline polymers requires further consideration. One has to examine the fate of the crystalline components, also. Are they retaining their identity? Or are they modifying one another due to the compatibilty of their corresponding amorphous and crystalline phases? Even if the polymers are thermodynamically miscible, crystallization may result in phase segregation. Thus, morphological features such as degree of crystallinity, domain shape, and size are affected by the relative rates of crystallization of the component polymers. Although effects are specific to the type of blends, some general observations can be made. The blending of a high melting polymer with a low melting polymer accelerates the crystallization of the high melting polymer, even at low levels. This has been observed by some workers [18-22] and can be attributed to enhanced nucleation.

Nadkarni et al. [19] studied the behavior of polyphenylene sulfide (PPS) and high density polyethylene (HDPE) blends. They observed an effect on the crystallization behavior and morphology of the component polymers due to the presence of the other component. The relative amounts of the two polymers also influenced the crystallization process. The morphological changes were similar for PET and PPS. These included larger crystalline size, a narrow crystalline size distribution, and reduced degree of crystallinity as compared with the pure polymers. The high melting PPS showed faster crystallization for compositions where PPS forms the major phase (by volume), whereas the overall crystallization rate was retarded beyond HDPE volume fraction of about 35-40%. It was hypothesized that the presence of HDPE melt increases nucleation but decreases the crystal growth of PPS. The retarding influence on the crystal growth would be more pronounced in blends with higher HDPE fractions and hence, a minimum is observed in the crystallization time of PPS with respect to HDPE volume fraction. On the other hand, the crystallization time of HDPE decreases gradually with the volume fraction of PPS (signifying higher crystallization rates). This was attributed to the presence of solidified PPS particles during the crystallization of HDPE, which can act as heterogeneous nuclei and accelerate the crystallization.

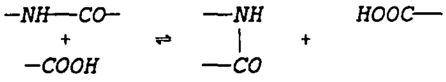
In binary blends of semi-crystalline polymers, a considerable rise in T_c of the major component due to the presence of the minor one with higher T_c has been reported [20]. The possible reasons suggested were the migration of nuclei across the interface, nucleating agent-like behavior of the already crystallized minor component, or altered chain mobility in the interface, or reduction in molecular weight upon processing. It should be noted that semi-crystalline polymer blends, containing one component with a higher T_c and dispersed as a fine suspension, sometimes exhibit retarded crystallization. Such retarded crystallization behavior has been reported for uncompatibilized blend systems such as nylon 6/polyvinylidene fluoride, polybutylene terephthalate/polyvinylidene fluoride, and polyethylene/polyoxy methylene. In these blends the dispersed droplet sizes were controlled by altering mixing conditions [20]. These observations are not completely explained, or the explanations are not satisfactory or contradictory. However, the technical importance of the retarded and coincident crystallization, the so called "concurrent crystallization", is obvious [21]. The lowering of the T_c, sometimes by several degrees, is significant. Moon et al. [22] studied the thermal behavior of polypropylene (PP) and nylon 6 (N6). The value of T_c is 117°C for pure PP and 181°C for pure nylon 6. The T_c rises remarkably to 125°C and 195°C for PP and N6, respectively, in noncompatibilzed blends. The addition of a compatibilizing agent, maleic-anhydride grafted polypropylene (MAH-g-PP), does not exert any noticeable change on the T_c of PP but decreases the T_c of N6. As the concentration of MAH-g-PP is increased, the crystallization peak corresponding to N6 T_c eventually disappears. The addition of MAH-g-PP fractionates the crystallization of N6 - one is at N6's T_c and the other at PP's T_c. The addition of 1.5 phr (parts by weight of additive per hundred parts) MAH-g-PP can induce almost complete concurrent crystallization of N6 and PP.

3.3 Reactive Blends

3.3.1 Polyamide/Polyamide

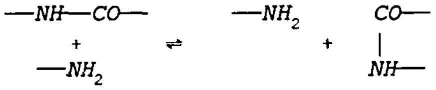
So far the discussion has been restricted to purely physical effects. It is entirely possible that the components can interact or react with each other. Here the actual chemical structure of the polymers comes into play. It is well known that interchange reactions occur in condensation polymers, such as polyesters, polyamides and polycarbonates [23-36]. However, very little information is available in the open literature about interchange reactions in polyamide/polyamide blends [23-29]. An excellent review of the available information has been provided by Kotliar [23]. The information does not give a definitive answer as to the mechanism of transamidation. However, clearly, the following possibilities exist:

Acidolysis :



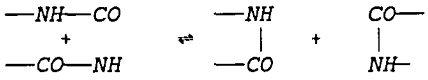
$$\begin{matrix}-NH-CO- \\ + \\ -COOH\end{matrix} \rightleftharpoons \begin{matrix}-NH \\ | \\ -CO\end{matrix} + HOOC-$$

Aminolysis :



$$\begin{matrix}-NH-CO- \\ + \\ -NH_2\end{matrix} \rightleftharpoons -NH_2 + \begin{matrix}CO- \\ | \\ NH-\end{matrix}$$

Amidolysis :



$$\begin{matrix}-NH-CO \\ + \\ -CO-NH\end{matrix} \rightleftharpoons \begin{matrix}-NH \\ | \\ -CO\end{matrix} + \begin{matrix}CO- \\ | \\ NH-\end{matrix}$$

The first two reactions, acidolysis and aminolysis, are due to the reactions of the end-groups on one polyamide with an amide group on the chain of the other polyamide. Hence, these reactions are influenced by the concentration of end-groups as well as the molecular weight. Reaction of the amide group on one polyamide with an amide group on the other polyamide is called amidolysis. Research done by Miller [24] showed that amidolysis was insignificant as compared to the other two reaction methods. However, this work was done with model compounds which were low-molecular weight materials. It should be noted that any of these reactions will lead to the formation of a block copolymer.

The actual process of melt blending is schematically shown in Figure 3.3 [25]. In the beginning, the homopolymers are present in the ratio in which they were mixed. These are represented as the stiff (semi-crystalline) polymer and the flexible (amorphous) polymer. Reaction in the initial stages results in large blocks of the flexible polymer being interchanged onto the stiff polymer. These blocks break into smaller blocks at intermediate stages and into a random copolymer at the final stage. The actual structure of the random copolymer is directly related to the composition of the mixture. Through all stages, the chemical composition of the blend remains constant, the same as the initial ratio. It is merely the size and distribution of blocks that change. Figure 3.4 [18] shows the experimental change in the composition of a nylon 6/nylon 6,6 mixture during the melt blending process. The change in the amount of homopolymers, block copolymer and random copolymer can clearly be seen. After two hours of melt annealing, no homopolymer remains, 90% is block copolymer and 10% is random copolymer. From that point onwards, the amount of block copolymer decreases and the random copolymer increases. Hence, the reaction time is a critical factor in determining the final structure of the blend.

It is well known that interchange reactions in polyamide blends are very slow. It takes

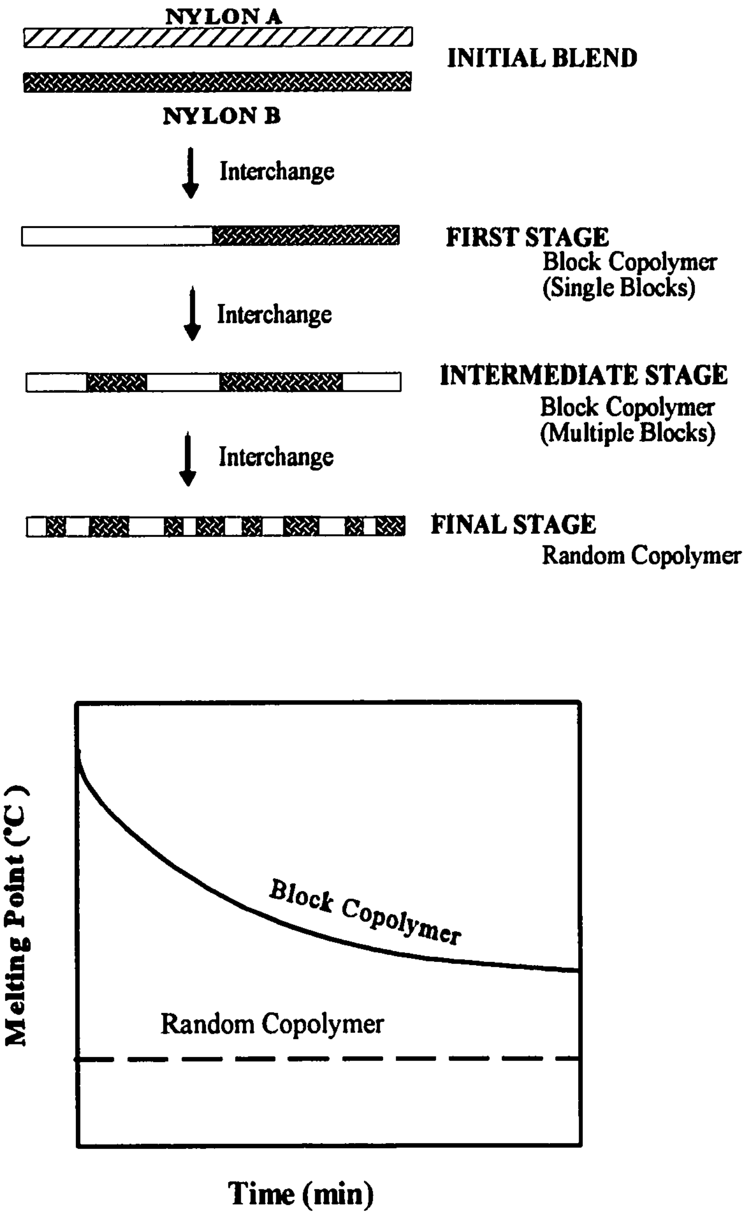


Figure 3.3: Schematic representation of the melt blending process of two nylons - showing the structure of copolymers formed with time, as a result of interchange reactions, and the effect on the melting point.

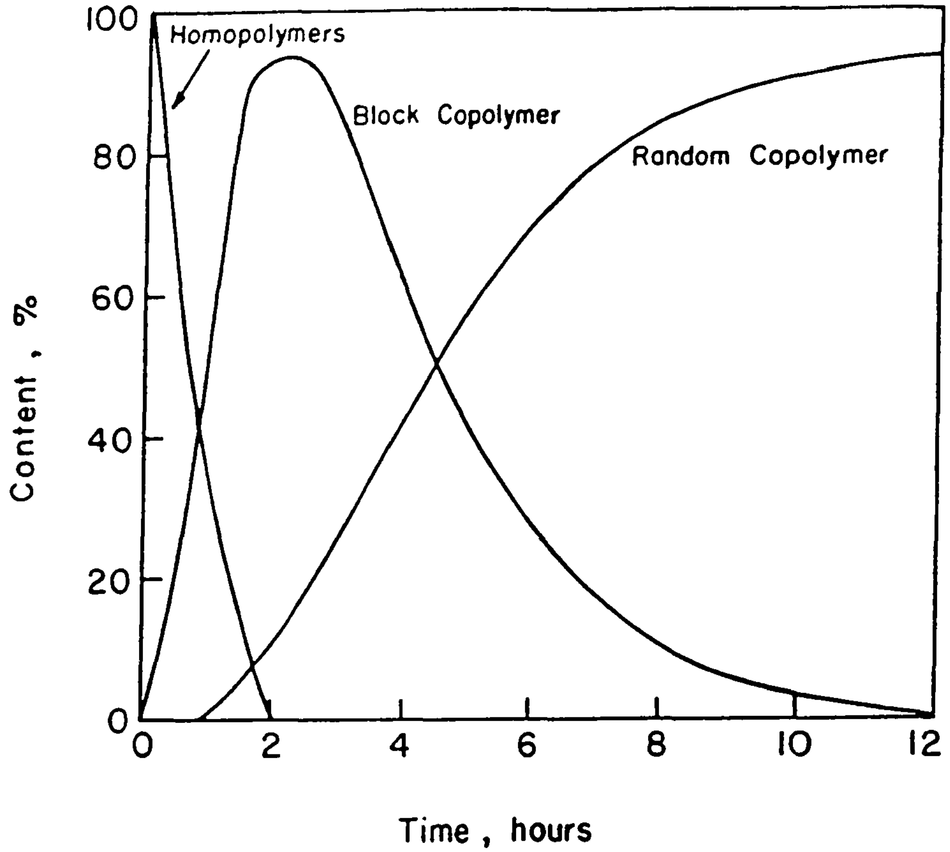


Figure 3.4: Variation in the composition of nylon 6,6/nylon 6 mixture during the melt blending process. [V.V. Korshak and T.M. Frunze, "Synthetic Hetero-Chain Polyamides, " p. 258, printed in Israel by S. Monson, Jerusalem]

more than 8 hr at 285°C to achieve true randomness for nylon 6 and nylon 6,6. Evidence for block copolymer formation has been obtained by measurement of solubility and melting point changes. Figure 3.3 shows the schematic change in melting point due to the change in block length. Quantitative techniques, however, are lacking for measurement of either degree of amide exchange or segment length in block copolymers. However, monitoring change in T_m is a possible method by which the extent of reaction can be measured indirectly, with the T_m of the random copolymer (can be estimated theoretically) marking complete conversion. The formation of block copolymers has a pronounced effect on crystallization. If one homopolymer is semi-crystalline and the other amorphous, non-crystallizable sequences will be built in between the crystallizable sequences of the semi-crystalline polyamide. This leads to a decrease in the crystallization rate of the blend, as compared with the crystallizable homopolymer. The degree of suppression can be controlled by the extent of reaction, which directly relates to the structure of block copolymers actually present. Similar effects are seen, though not of the same magnitude, if both the homopolymers are semi-crystalline, since the lengths of the crystallizing units could be different in the two polyamides. The change in structure is also expected to decrease the degree of crystallinity

Phase homogenization (miscibility) caused by interchange reactions results in a significant decrease in crystallizability as the material approaches a random copolymer, as reported by Takeda and Paul [26,27]. They showed that melt blends of poly(m-xylene adipamide), an amorphous nylon, and Nylon-6, prepared by extrusion at 260°C, have two glass transitions and are opaque. Whereas similar preparation at 290°C yielded transparent blends and a single glass transition temperature, suggesting that transamidation leads to the formation of miscible blends. The phase homogenization was shown by means of thermal, dynamic mechanical, and nuclear magnetic resonance analyses to be the result of interchange reactions. A single phase developed after as few as five interchange reactions per molecule. Physical homogenization can be achieved by relatively few interchange reactions when the physical interaction energy between the two starting materials is relatively small, i.e., near miscibility. For blend components far from miscibility, the extent of interchange reaction would have to approach a structure similar to a random copolymer before phase homogenization would occur.

It has been discussed that the formation of block/random copolymers as a result of transamidation reactions leads to significant reductions in T_c, which is the primary goal of this research. However it is absolutely necessary to look at how the physical and mechanical properties of block copolymers compare with those of the corresponding random copolymer and homopolymers. The important properties of T_m, T_g, tensile strength, modulus and elastic properties depend on the structural arrangement of the molecular units comprising the polymer structure. All available data suggest that properties of block copolymers are superior to those of random copolymers. A block copolymer can have properties of the homopolymers as well as a set of properties reflecting the overall polymer structure.

Table 3.1 [reproduced from ref. 25] shows the properties of block versus random copolymers prepared by melt blending of nylon 6,6 and poly(metaphenylene adipamide). Clearly, the block copolymers have better modulus, cold growth, and set properties without a loss in other properties such as tenacity and elongation. There is, for example, reduced flat spot depth of tire cords made from the block copolymers versus the random copolymer and pure nylon 6,6. Zimmerman et al. [28] described the reinforcement of nylon 6,6 by blending with stiff, high-T_g polyamides at low degrees of amide interchange. This unusual reinforcement was beyond that which can be expected on the basis of existing reinforcement theories. In general, random copolymers should be avoided as they exhibit poor physical properties. Figure 3.5 [25] shows the variation in tensile strength of a nylon 6,6/nylon 6 copolymer during the melt blending process. It can clearly be seen that tensile strength decreases as a function of melt blending time, indicating the loss in strength of the copolymer formed at the latter stages, due to increased randomization taking place with time.

Table 3.1. Properties of Pol(hexamethylene adimapide)/Poly(metaphenylene adimapide) Block Versus Random Copolymers*

Type	Tenacity g/den.	Elongation to break, %	Initial Modulus g./den.	Relaxed cold growth, %	Set, %	Flatspot, mils
Block (70/30)	8.7	17	100	1.4	0.56	117
Block (75/25)	7.0	10	70	2.3	0.68	127
Block (80/20)	7.1	12	75	2.6	1.04	157
Random (90/10)	7.6	13	68	3.7	1.45	190
Random (80/20)	3.1	15	46	5.7	2.3	263
Nylon 6,6 (100/0)	8.5	16	49	3.7	1.7	210

* British patent 98, 6377 (1963), E. I. Du Pont dc Numours.

Aliphatic polyamides are known to have good processability, high melting points and good mechanical properties. Aromatic polyamides, on the other hand, have a high glass transition temperature and reduced moisture update. Hence, there is an obvious advantage in blending these two materials [28,29], especially if the final morphology and physical

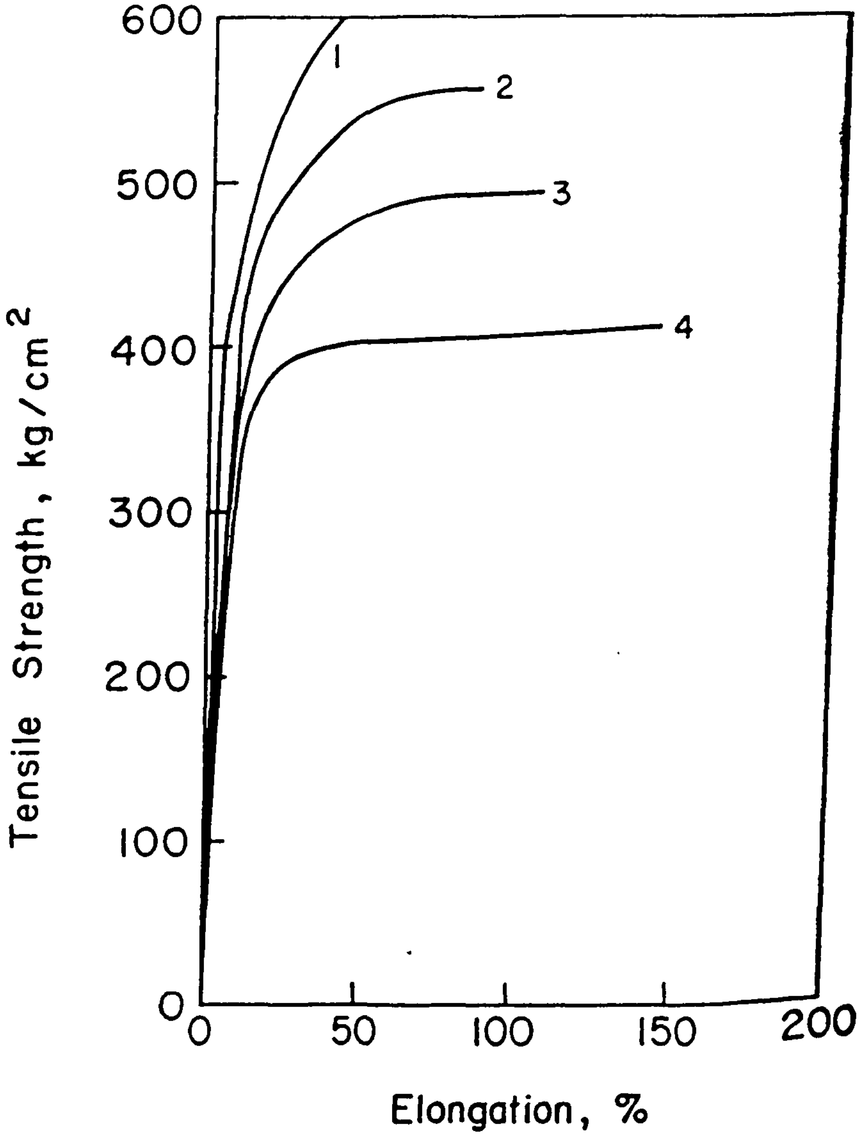


Figure 3.5: Variation in the tensile strength of nylon 6,6/nylon 6 copolymers as a function of melt blending time of (1) 0 hrs; (2) 2 hrs; (3) 4 hrs; (4) 12 hrs (from ref. 25)

properties can be controlled by the use of interchange reactions. Melt blending (and block copolymerization) with aromatic-aliphatic polyamides raises the modulus and reduces creep. Hence, there is a possibility of reducing “flat spotting” in nylon tire cords.

Little information is available on catalysts that can enhance these transamidation reactions. Transamidation of nylon 6 with nylon 6,6 has been performed at 280°C on a 1.25 inch Wayne extruder at ≤ 10 min residence time in the presence of 1% phosphite catalyst. The blend had a single T_m and a lower heat of fusion than either of the homopolymers [30]. Phosphite catalysts include triphenyl phosphite (TPP), tri-n-butyl phosphite or a mixture of the two. The mechanism by which the catalyst works is not clearly understood. However, it is known that viscosity can be built up in nylon 6,6 by coextrusion with alkyl phosphonic acid. Initial nylon inherent viscosity of 1.09 dl/g could be increased to 1.46 dl/g in the presence of 0.007 wt.% cyclohexyl phosphonic acid when the process was run in a 5 cm extruder at 60 rpm with 5 min residence time. Chain extension of nylons bearing both carboxylic acid and amine end groups by coextrusion with tertiary phosphite condensing agents has been reported [31]. There was a significant increase in intrinsic viscosity of nylon 6 when extruded at 300°C in the presence of 1% TPP. Among the 14 phosphites examined the rough order of reactivity was triphenyl > diphenyl > tributyl > triethyl > distaeryl pentaerythritol diphosphite [31]. Inorganic phosphites were found to be ineffective.

The formation of amide or ester bonds during melt-processing in the presence of organic phosphites was observed in various polymer and polymer blends, provided that (a) they contain available carboxylic groups and aliphatic amine or hydroxyl groups, (b) they are stable under the processing conditions, and (c) their melt viscosities are matched to allow thorough mixing during the melt blending. Aharoni [31] was successful in preparing block copolyamides within 5 mins at 300°C in the presence of 1% TPP. The polymer blends examined were - nylon 6/nylon 6,6, nylon 6/nylon 12, nylon 6/nylon 11, nylon 6/nylon 6T and nylon 6/Trogamid-T. It was also possible to prepare block poly(ester-amide) with blends of nylon 6 with PET, PBT and Kodar A-150.

In conclusion it needs to be said that not all nylon blends exhibit transamidation reactions. In nylon 6 and nylon 6IcoT blends [32], there was no evidence of significant transamidation during injection molding and annealing. Injection molded samples were homogeneous (single T_g) but annealing above T_g increases crystallinity and induced phase separation. In fact, crystallization of the nylon 6 component was greater than that of the pure nylon 6 in some blends.

3.3.2 Other Reactive Blends

Theoretically it is possible to find a number of polymers that can potentially react with nylons. In principle, any polymer possessing chemical groups that can react with an amine, acid or amide group, is a possibility. The focus, however, was on polymers that were chemically similar to nylons. Some of these reactive polymers are discussed below.

Pillon and Utracki [33] and Pillon et al. [34] prepared nylon 6,6/PET block copolymers through reaction of amine end groups with an ester linkage in the polyester chain. The process was run in either a Brabender mixer at 265-295°C for 10-35 min or a twin screw extruder at 290-370°C, 10-21 rpm and 2-4 min residence time. The catalyst used was p-toulene sulfonic acid (TSA; 0.2 wt.%). Maximum copolymer formation (23%) was obtained by extrusion with TSA at 350-370°C with 2 min residence time. Ester/amide reactions are generally believed to be slower than amide/amide reactions [23]. Blends extruded either without TSA or at less than 310°C showed no copolymer formation. This corroborates earlier work that had shown no copolymer formation in blends of PET with different types of nylons.

In a study [35] on the interchange reaction of nylon 6 with BPA polycarbonate, blends were prepared in a Brabender mixer at 240°C, 30 rpm with 15 and 45 min residence time. Evidence for copolymer formation was obtained by selective extraction, IR spectroscopy, and thermal analysis. SEM's showed that discrete PC domains were present at 75/25% nylon/PC blend after 15 min residence time but the blend appeared homogeneous after 45 min as a consequence of increased copolymer formation. Motaudo et al. [36] showed that interchange reactions occur above 300°C, and that only the cleavage of carbonate groups, by means of nylon 6 amino end groups, is actually occurring at 240°C.

Nylon/anhydride modified ethylene-propylene rubber (EPR) are commercially available compatibilized blend systems, used to improve the toughness and impact resistance of the material. A maleic anhydride grafted EPR can undergo an imidization reaction with the polyamide, as illustrated in Figure 3.6 [10]. Similar reaction is produced for the case of an acid grafted material. Maleic anhydride modified EPRs are commercially available, for example, Exxelor products from Exxon. Other workers [10] have examined blends of polyamides with styrene-maleic anhydride copolymer (SMA), as a means of improving mechanical and thermal properties. A 12°C increase in heat distortion temperature was obtained with the addition of 15% by weight of SMA. Melt viscosity and elasticity were also increased on SMA addition. All these effects were attributed to an anhydride-amine reaction.

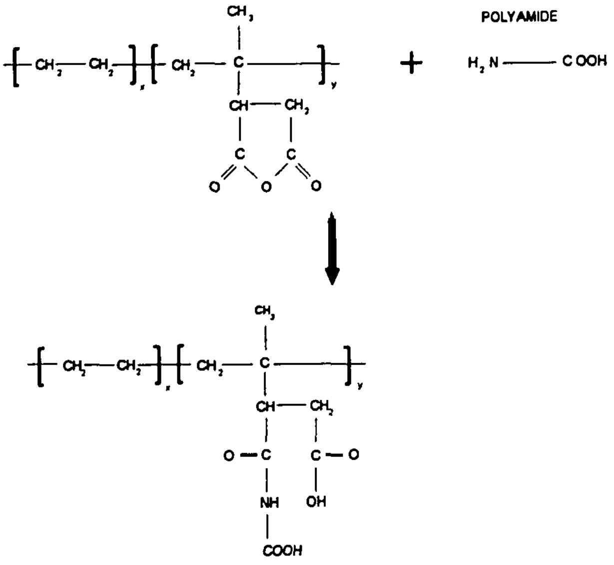


Figure 3.6: Schematic of the reaction between maleic anhydride and polyamide

CHAPTER 4

EXPERIMENTAL DESCRIPTION

4.1 Materials

A list of materials used and their source is provided in Table 4.1. Three different sources of nylon 6,6 were used in preparing the blends. Initially, solution blending was done with nylon 6,6 from Scientific Polymer Products. Extrusion grade nylon 6,6 was purchased from Dupont (Zytel 101) for melt blending work with the Maxwell extruder. Once the nylon 6,6 was received from Rhodia Inc., further blending work was done with that material. Chapter 5 compares the thermal behavior of these three types of nylons and Table 5.1 reports the type of nylon 6,6 that was used in preparing each blend.

TABLE 4.1: LIST OF MATERIALS USED

	MATERIAL	SOURCE OF MATERIAL
1.	Nylon 6,6	Scientific Polymer Products Rhodia Zytel 101, Dupont
2.	Nylon 6(3), T or Poly (trimethyl hexamethylene terephthalamide)	Scientific Polymer Products
3.	Nylon 6,12	Scientific Polymer Products
4.	Zytel 330	Dupont
5.	Trogamid-T®	Huls America
6.	Polyethylene Glycol (Carbowax® PEG 20 M)	Union Carbide Chemicals & Plastics Company, Inc.
7.	Polyacrylic Acid (M.W. 450,000)	Polysciences
8.	Polyethylene Oxide	Polysciences
9.	Polystyrene Sulfonate (M.W. 70,000)	Scientific Polymer Products

TABLE 4.1: LIST OF MATERIALS USED

10.	Separan AP30® Polyacrylamide	Dowell R & D
11.	Nylon 6	Scientific Polymer Products
12.	Polymethylmethacrylate (PMMA)	Polysciences
13.	Nylon 12	Scientific Polymer Products
14.	Polycarbonate (BHPP 801)	GE Plastics
15.	Polyphenylene Ether (BHPP 820)	GE Plastics
16.	Exxelor PO1015 (Maleic Anhydride)	Exxon Chemicals
17.	Hypermer FP4 (contains anionic polyester)	ICI Americas, Inc.
18.	Silicone Oil	Fisher Scientific
19.	Formic Acid (90% vol/vol)	Fisher Scientific
20.	Meta-cresol	Fisher Scientific
21.	Adipic acid (99%)	Aldrich
22.	Triphenyl phosphite	Aldrich
23.	Chromic acid	Fisher Scientific
24.	Acetone	Aldrich

The twin screw extruder (described later) was flushed with argon (WV Welding) for all extrusion runs. Initial DSC runs were made with regular nitrogen (WV Welding) flush which was replaced with high purity nitrogen (99.9999%, WV Welding) during the detailed experimentation stage. The extruders were cleaned with adipic acid (99%, Aldrich). Preliminary work was carried out with triphenyl phosphite (Aldrich) as a catalyst for accelerating the interchange reactions. Initial solution blending work was done with meta-cresol (Aldrich) which was replaced with formic acid (Aldrich) in the later stages.

4.2 Solution Blending Procedure

Even though it was known that the chosen additive should have the ability to melt blend with nylon 6,6, solution blending was still carried out. There were several reasons for doing this:

(I) The procedure is convenient for obtaining small samples needed for DSC work.

(ii) Melt blending of small samples is often beset by poor mixing; here mixing on a molecular scale is assured.

(iii) Melt blending results are sometimes different from solution blending results. Solution blending was carried out to ensure that a promising additive was not missed out because the mixing technique used was not an effective one.

(iv) Some commercial polymers can be solution blended but not melt blended. If these produced the desired results, then custom-made structurally similar polymers that were melt blendable could be examined.

(v) Solution blending results could be useful for mechanistic and theoretical reasons. Additionally, results could be obtained fairly quickly with solution blending, while the melt blending technique was being perfected and standardized.

Solution blending involved dissolving nylon 6,6 and the chosen additive in a common solvent; initially this was m-cresol. The actual procedure was to dissolve separately each polymer by slowly stirring on a hot plate (60-70°C) for as much as 1-2 days. Concentration levels of 0.4 - 1.0% wt./vol. were employed. The two solutions were then mixed in the desired proportion, and the solvent was removed by evaporation in a rotary vacuum evaporator, using the setup shown in Figure 4.1. The mixed solution was placed in the

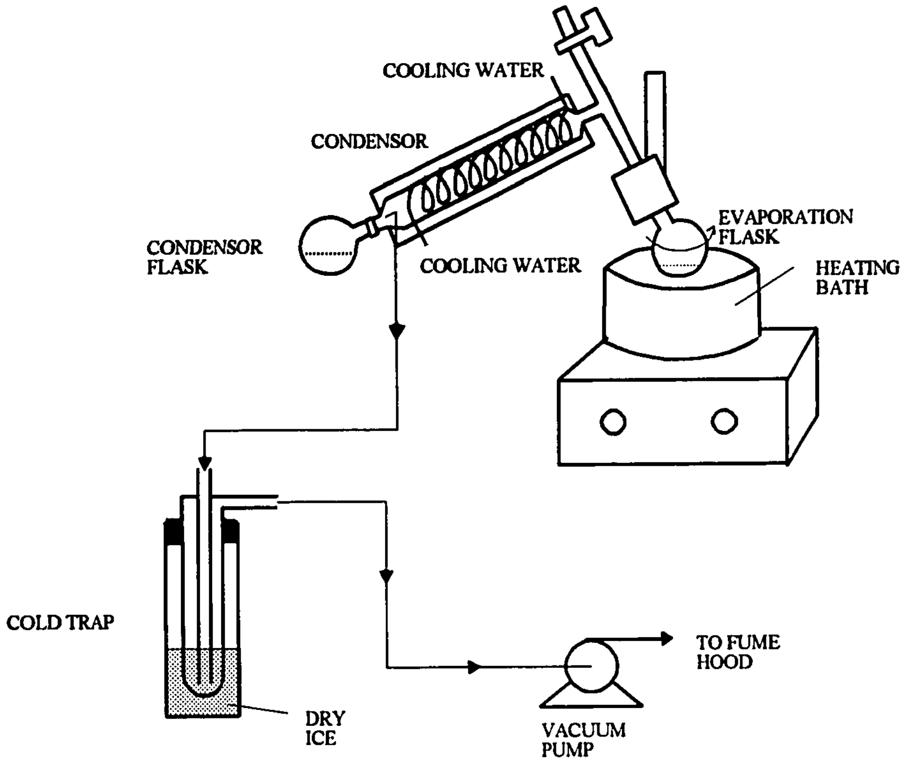


Figure 4.1: Vacuum rotary evaporation setup used for removal of the solvent from nylon 6,6 blends

evaporation flask. As the temperature of the bath increases, solvent evaporates and is condensed in the condenser and finally collected. The non-condensed vapors make their way into the cold trap, which serves the purpose of condensing that vapor and preventing it from getting into the vacuum pump. The cold trap is maintained at a temperature of -16°C by using dry ice. The freezing point of water is 0°C while both formic acid and m-cresol freeze around -5°C. The outlet from the pump was placed inside the fume hood to dispose of any toxic vapors.

At these concentrations, no gelling was observed when the two solutions were mixed. The blended solution was initially heated to 60-70°C to remove any water present as this can cause bumping of the solvent. The solvent was then removed at 120-140°C under a vacuum of 29 inches of Hg. To minimize oxidation, lower temperatures (30-40°C) were used at the end of the evaporation step which lasted for a total of 5-8 hours. Finally, the concentrated solution was dried in a vacuum oven at 40-60°C for 2-3 days before testing. The total yield was 0.2-0.5 g of polymer blend.

As work progressed, formic acid was substituted for m-cresol due to problems associated with the toxic nature of the latter solvent. The setup remained the same, but polymer concentrations of 1-2% could now be used due to the ease of dissolution. Further, since formic acid (bp = 101°C) is more volatile than m-cresol (bp = 203°C), lower evaporation temperatures of 70-80°C were used. In addition, drying was accomplished in the rotary evaporator itself in only 2-3 hours.

Some polymeric additives were more easily dissolved in water. In this case, the aqueous solution of the additive was mixed with nylon 6,6 dissolved in formic acid, and the water removed by evaporation at room temperature.

4.3 Melt Blending Procedure

Two types of extruders were used - Maxwell and twin screw. These are described below:

Maxwell Extruder: Initial melt blending work was carried out on a custom-built Maxwell extruder [37]. This is shown in schematic form in Figure 4.2 and is similar to a commercial device marketed by Custom Scientific Instruments. The machine does not have a screw and it works due to the presence of normal stresses. The material is conveyed through the machine by the centripetal pumping action developed as the result of rotary shearing of viscoelastic melts. Normal forces are developed when a viscoelastic material is sheared between a rotating bob and a stationary plate, and the magnitude of these normal forces depends on the elasticity of the melt. Since the gap between the bob and the plate is fixed, these forces cause the molten material to be extruded through the die in the plate. This is referred to as *elastic melt extrusion* or *rheoelastic extrusion.*

In general, as the rate of shear of the melt is increased, the response of the material becomes more elastic and hence the pumping action is improved. The shear rate is controlled by varying the rate of rotation of the bob and the gap between the bob and the plate. The actual pressures developed in this type of extruder depend on the elastic nature of the material as well as the shearing rate. It was observed that extrusion of materials with low elasticity is difficult on this extruder. Advantages include small sample size (of the order of 10 g), good temperature control and a short residence time. Also there is no necessity of drying the

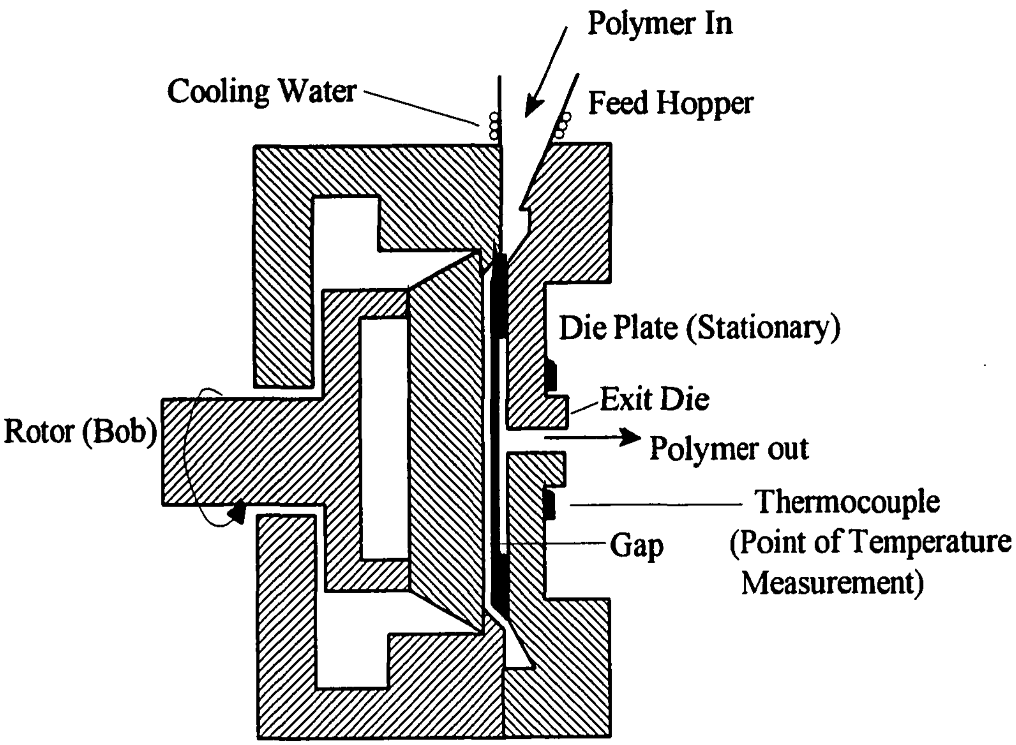


Figure 4.2: Schematic view of the Maxwell extruder showing the rotating bob, stationary plate and the gap where the molten polymer is sheared

polymer since degassing takes place in the thin film that forms between the bob and the die plate.

Significant experimentation was needed to determine conditions that would yield a continuous extrudate of nylon 6,6 that showed no visible signs of thermal degradation. A nitrogen purge had to be used, and the temperature was set at 260°C; this may or may not have been the actual melt temperature. The temperature is measured on the outside of the die plate, as indicated in Figure 4.2. Even so nylon 6,6 from Rhodia could not be easily extruded due to the large pellet size; powders were much easier to process. Thus, all the melt blending work was done using nylon 6,6 obtained from Dupont, which had the smaller pellet size.

Blending Procedure: First, pure nylon 6,6 was extruded, followed by about 10g of a mixture of nylon 6,6 and the additive. This was followed, in turn, by pure nylon 6,6. A typical run lasted for approximately 3-4 minutes and the die exit was periodically blocked to increase the residence time and improve mixing uniformity. Uniformity was a major concern especially at low additive concentrations, since, often a few large pellets with a large number of small pellets were being blended. A large residence time was not possible due to polymer oxidation or degradation as well as problems in extrusion itself.

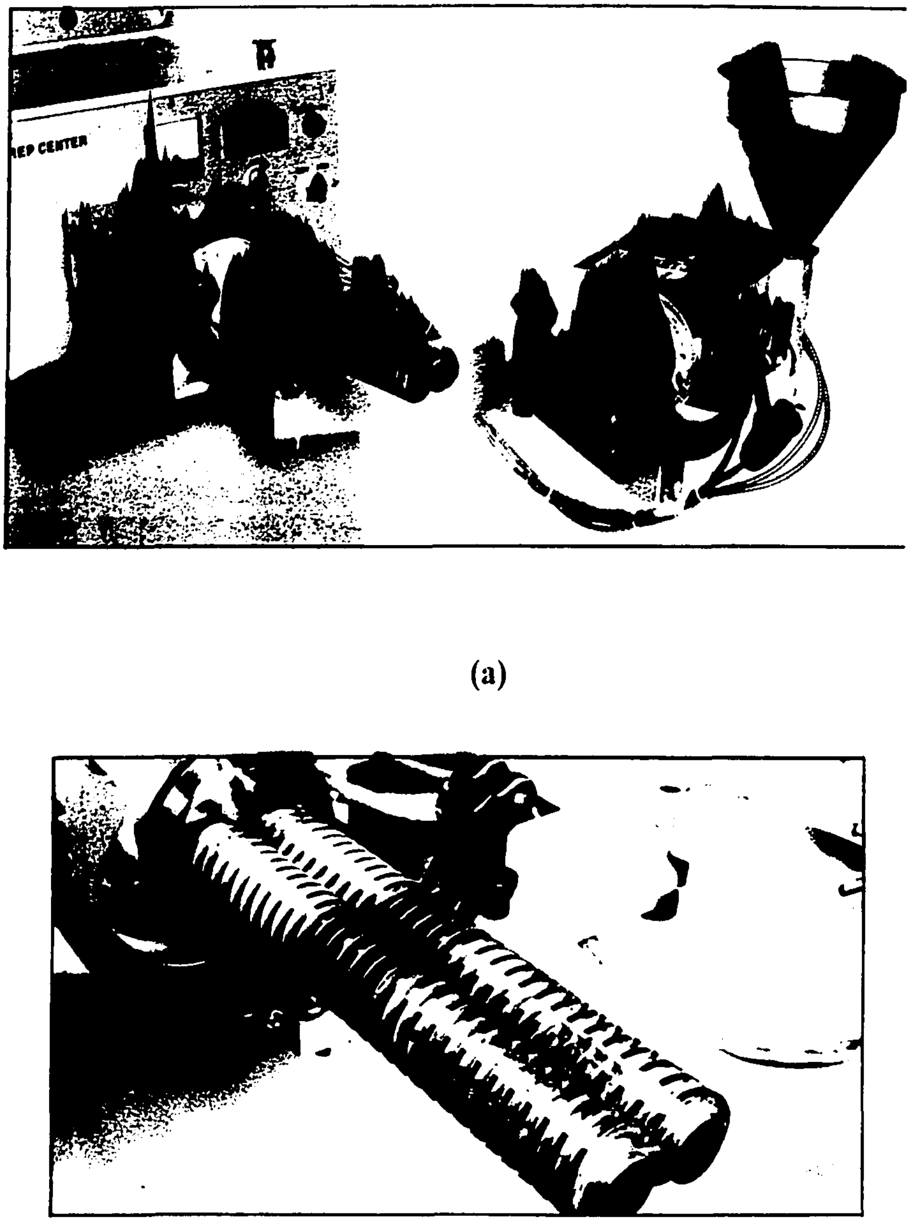
Not every melt-processable additive could be blended with nylon 6,6 in the Maxwell extruder. Since the extrusion temperature was fixed by the behavior of pure nylon 6,6, additives having a significantly higher melting point could not be used as these would not melt at the temperature of operation. Similarly, materials with a significantly lower melting point could not be utilized as these had very low melt viscosity; worse, several fumed or degraded. Even when a polymer, such as polymethyl methacrylate, could be extruded alone at the selected temperature, it sometimes would not extrude easily along with nylon 6,6. All this severely limited the choice of additives that could ultimately be tested.

For polymers which could be blended with nylon 6,6, a long strand (diameter of 1/8-1/16th inches) of the mixture was extruded. Only the central portion of this strand was subjected to thermal characterization in the expectation that this part would have the desired composition.

Twin Screw Extruder: A twin screw extruder (model D6/2, C.W. Brabender Company) was used for blending polymeric additives with nylon 6,6 (Figure 4.3). The extruder features single flighted, counter rotating, intermeshing 42 mm diameter screws and a 276 mm long barrel. As Figure 4.3 shows, the screws are short but there are gaps in the screws which promote backmixing and increase the residence time. It can extrude at rates upto 10 lbs/hr with a minimum sample size of 200 g. The hopper was modified to provide an argon atmosphere and easy visible batch feeding. Different extruder nozzles had to be machined in-house in an attempt to obtain different residence times.

Drying: This was carried out in a vacuum oven (Hotpack Company). The oven has a special attachment which allows it to be operated at temperatures as high as 300°C. A vacuum gage (Kurt J. Lester Co.) capable of reading in the 0.1-20 torr (mm Hg) vacuum range was installed into the exit port of the oven. A high vacuum pump (Trivac, Kurt J. Lester Co.) was used.

The drying was carried out at 100°C at the maximum vacuum obtainable (0.4-0.6 mm Hg absolute pressure). The temperature was first set at 100°C without any vacuum. Once the desired temperature is reached, the pellets are introduced into the oven and the vacuum



(a)

(b)

Figure 4.3: Twin Screw Extruder, model D6/2 (C.W. Brabender Company); (a) view of the open extruder, (b) view of the screws showing the backmixing sections

applied. This condition is maintained for the desired period of time. At the end of that time period, vacuum is broken and the pellets withdrawn and directly used for extrusion. Alternatively, the pellets can be stored in the oven at room temperature, under vacuum, until the extruder is ready to be operated.

Typical Extrusion Run: The heaters are set to the desired temperature, typically 253°C, 263°C, 264°C, 267°C were used for the four heating zones, respectively. The extrudate temperature was not equal to 267°C because of viscous heating and heat losses at the die surface. A lower temperature was used in the first section to prevent melting in the hopper. Temperatures were increased slightly to allow for easy extrusion, since it was noticed that low temperatures in the later section hampered smooth extrusion. The water supply to the hopper is started, to ensure that the pellets do not melt in the hopper and block the feed port. The argon purge is started to expel the air present in the hopper. Compressed air at 12-15 psi is run to the extruder to cool the different heating zones and hence maintain the temperature.

It takes close to 30 min for the extruder to reach the set temperatures. Extrusion is started only after the temperatures have stabilized. First the high density polyethylene (HDPE) remaining from the previous shutdown is flushed by extruding pure nylon 6,6. At this stage the premixed blend (prepared by weighing desired amounts of nylon 6,6 and the additive) is fed into the hopper. The weighed pellets are tumble mixed in a container. The pellets need to be dried just before extruding the blend to eliminate any storage time where moisture could be picked up. Sufficient amount of the blend needs to be added to ensure that the contents of the extruder are completely flushed out. Once this has been achieved, the extrudate is collected in a container of cold water, to minimize oxidation of the molten polymer. The extrudate is then dried in the vacuum oven at 70°C and the dried polymer is stored in the dessicator (Thomas Scientific) which maintains relative humidity at 20-30%.

The extruder is shutdown by flushing it with HDPE. After sufficient HDPE has been extruded, the temperatures are decreased to about 200°C with the extruder running. Once this temperature is reached, the motor is shutoff first, followed by the heaters. The water supply to the hopper is shut off as well as the argon purge. The air supply to the extruder is also shut off. It takes close to two hours for the extruder to cool down to room temperature.

Cleaning: The extruder is shutdown with HDPE while it is still hot. Material is mechanically cleaned while the extruder is still being heated. The screws, barrel and the die are cleaned until they are relatively free of any clinging material. Then the following procedure is followed:

(1) Screws are removed and the trapped polymer is burnt in a furnace at 450°C for about 3 hrs. The residue is dusted/washed off. The surface is then lightly sandpapered. This leaves the screws relatively clean.

(2) Barrel and the die assembly are cleaned with adipic acid at 200°C by pouring the adipic acid powder on the hot metal surface and cleaning it with a clean cotton cloth. This cleaning is done repeatedly to remove as much of the degraded material as possible. The surfaces are finally cleaned with a fine sandpaper.

The cleaned extruder is run with HDPE for close to 15 mins before actual runs are commenced.

4.4 Intrinsic Viscosity Measurements

The intrinsic viscosity (IV) of nylon 6,6 and the blends was measured according to the method ISO-307, by the determination of the viscosity number. This involves the measurement at 25℃ of the drainage times of the solvent and of the solution of the polyamide at a concentration of 0.005 g/ml (0.5 g/dl, where 1 dl=100 ml), the same viscometer being used for both measurements. The viscosity number [η] (of a polymer) is given by the formula:

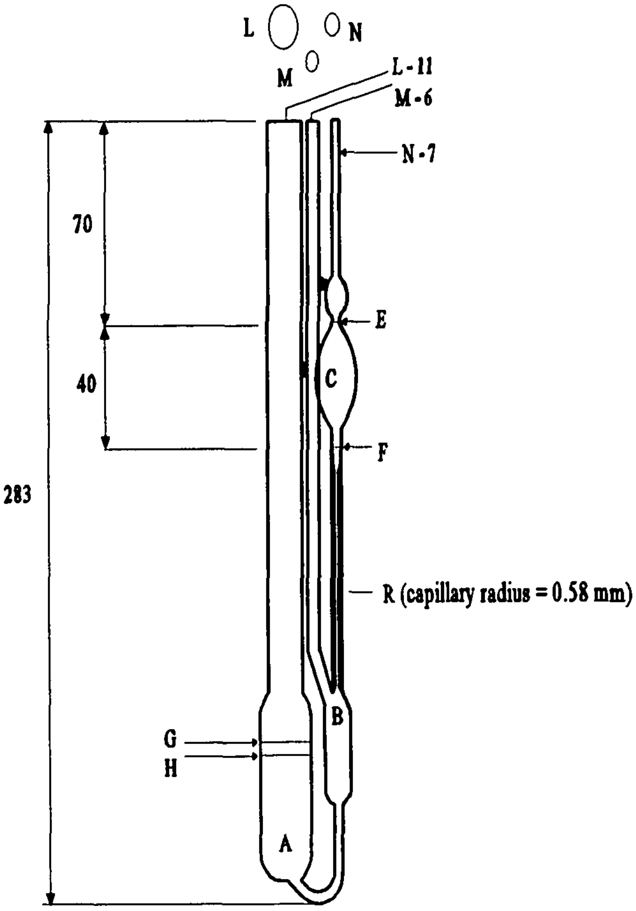
$$\left(\frac{\eta}{\eta_0} - 1\right)\frac{1}{g_p} \qquad \ldots(2)$$

η : *viscosity of solution*
η_0 : *viscosity of solvent*
g_p : *concentration of solution, in g/dl*

The viscosity number is usually expressed in milliliters per gram (100×deciliters per gram). It can be related to molecular weight of nylon 6,6 by the following relationship:

$$[\eta] = KM^a \qquad \ldots(3)$$
$$\text{where } K = 11\times10^{-4}\ ;\ a=0.2 \quad (\textit{ref.}\ [1])$$

Apparatus: A suspended level Ubbelohyde type viscometer (size 1, Cole-Parmer) was used. The essential dimensions of the viscometer are shown in Figure 4.4, adhering to the ISO-307 requirements. The inside diameter of the tube is 0.58±2% mm and the viscometer constant is 0.0750 centistokes/second. Formic acid (90% ± 0.15% wt/wt, Fisher Scientific) was used as the solvent. A container to serve as the thermostating bath was custom-built. A heater/refrigerator (Isotemp, Model 901, Fisher Scientific) circulates water to the bath to maintain the temperature at precisely 25°C. A stopwatch, accurate to 0.01s, was used. However, the human response time is only accurate to 0.1s. The entire setup is shown in Figure 4.5. The Isotemp circulator pumps water to the bath, the outlet being kept at the



All dimensions are in mm

Figure 4.4: Suspended level Ubbelohyde viscometer (size 1, Cole-Parmer) used for determining the drainage times of nylon 6,6 and its blends

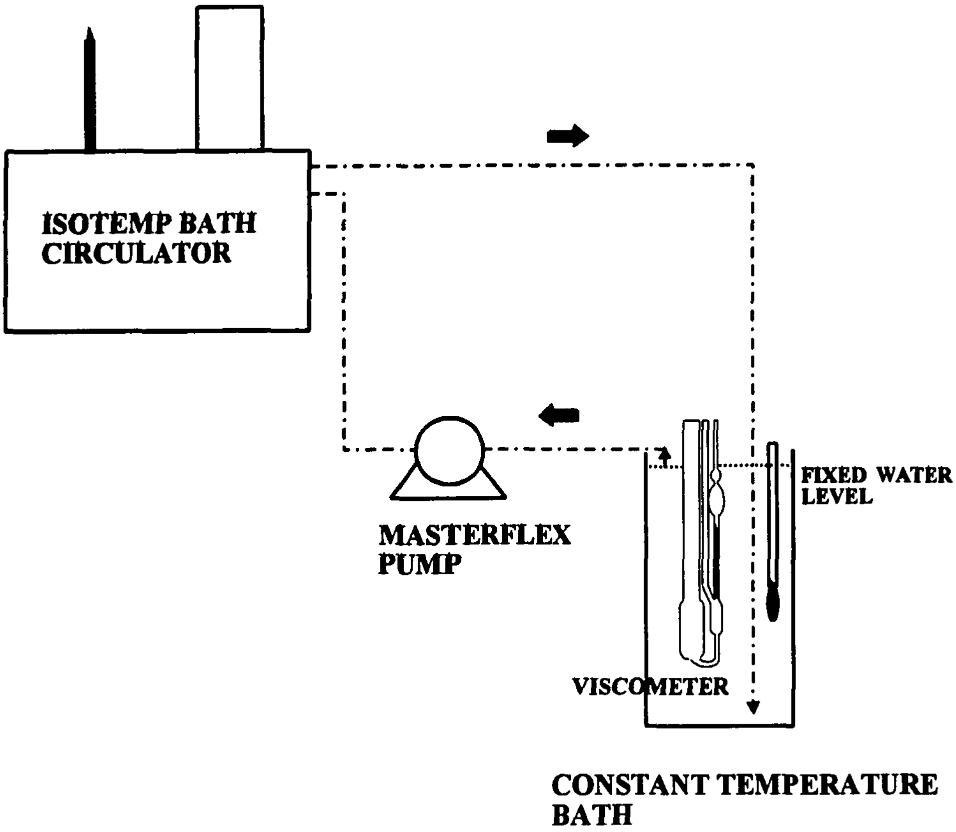


FIGURE 4.5: Intrinsic viscosity setup showing the constant temperature bath enclosing the viscometer and the circulation system used to maintain a constant temperature and water level in the bath

bottom of the bath. A masterflex pump is used to return the water from the top of the bath to the Isotemp circulator. By pumping at a faster flow rate than the circulator, the level of the water in the bath can be maintained at all times.

Measurement of drainage times: A 0.005 g/ml solution is prepared by dissolving 250.000 ± 0.005 mg of the polymer in exactly 50 ml solvent, measured using a volumetric flask. The sample is dissolved on a magnetic stirrer with the solution being contained in a closed flask to prevent any possible loss of the volatile solvent. It takes 3-4 hrs for the dissolution to be complete, depending on the size of the pellets/extrudate. No heating was used during the preparation of the solutions since it can affect the IV readings.

The solution is filtered through a sintered (fritted) glass filter (Fisher Scientific) to remove any small suspended particles which can affect the drainage time readings. These particles can appear due to contamination or could be present in the samples itself. The filtered solution is poured into the viscometer until the level lies between the filling marks. The filling should preferably be conducted outside the bath to prevent any possible contamination of the bath. The viscometer is mounted in the bath, which is maintained at 25°C. It should be ensured that the tube N is vertical and that the upper graduation mark, E (see Figure 4.4), is at least 30 mm below the surface of water in the bath. At least 15 min are allowed for the charged viscometer to attain the temperature of the bath.

Tube M is closed, allowing the liquid to be drawn into the upper bulb of tube N using a rubber bulb. Tube N is closed. Tube M is opened so that the liquid starts dropping from the lower end of the capillary tube. Tube N is opened and the drainage time is measured, to the nearest 0.2 s, for the time taken for the bottom of the meniscus to pass from mark E to mark

F. The measurements are repeated until two successive readings agree within 0.25%. If two successive readings differ more than 0.4 s, the viscometer is cleaned.

Cleaning: The viscometer is cleaned, prior to the first use, and after discordant readings, and, at intervals during regular use. It is allowed to stand for 12 hrs filled with chromic acid. The cleaning agent is removed, the viscometer rinsed with water, then with acetone and dried by passing a slow stream of filtered air through the viscometer.

4.5 Thermal Characterization

A TA Instruments model 2100 differential scanning calorimeter (DSC) with a 910S cell was used to characterize the individual polymers and their blends. DSC is a technique [38] used to measure the difference in energy inputs into the sample and the reference material as a function of temperature. Both the reference and the sample material are subjected to the same controlled linear heating or cooling rates. The TA instrument is a power-compensated type of DSC. The DSC contains constantan discs as the primary source of heat transfer to the sample and reference positions and as one element of the temperature measuring thermoelectric junctions. The sample and reference are placed in aluminum pans that sit on raised platforms on the constantan disc. The differential heat flow to the sample and reference is monitored by chromel-constantan area thermocouples formed by the junction of the constantan disc and a chromel wafer that covers the underside of each platform. Chromel and alumel wires are connected to the underside of the chromel wafers, and the resultant chromel-alumel thermocouple is used to monitor the sample temperature directly. Difference in power inputs to the two discs is computed and displayed in mcal/s or mJ/s and is an absolute measure of the endothermic or exothermic behavior of the sample.

The two techniques of thermal measurement primarily used in this work are isothermal and non-isothermal runs. A typical non-isothermal run is shown in Figure 4.6, illustrating the common thermal transitions.

Procedure

The procedure for obtaining the non-isothermal thermograms for nylon 6,6 and its blends is as follows:

- Equilibrate at 30°C.
- Ramp to 300°C at 10°C/min.
- Isothermal at 300°C for 5 mins
- Ramp to 50°C at 5°C/min

Additional runs involved heating at 10°C/min and cooling at 5°C/min again. Due to lack of a liquid nitrogen cooling accessory, higher cooling rates could not be used. A lowering of the T_c value below that of the pure component value of approximately 236°C was taken as an indication of the success of the blending operation - larger the reduction in T_c, more effective the polymer modifier. Other variations on the standard procedure included examining the influence of different cooling rates on the T_c value and the crystallinity developed during a non-isothermal run.

In a limited number of instances, isothermal and quenching experiments were also conducted. To measure isothermal crystallization rates (or times) the blend was heated to 300°C and held there for 5 mins (to destroy all crystallites). Then it was rapidly cooled to a temperature above T_g and held there isothermally until crystallization was complete. Lack of

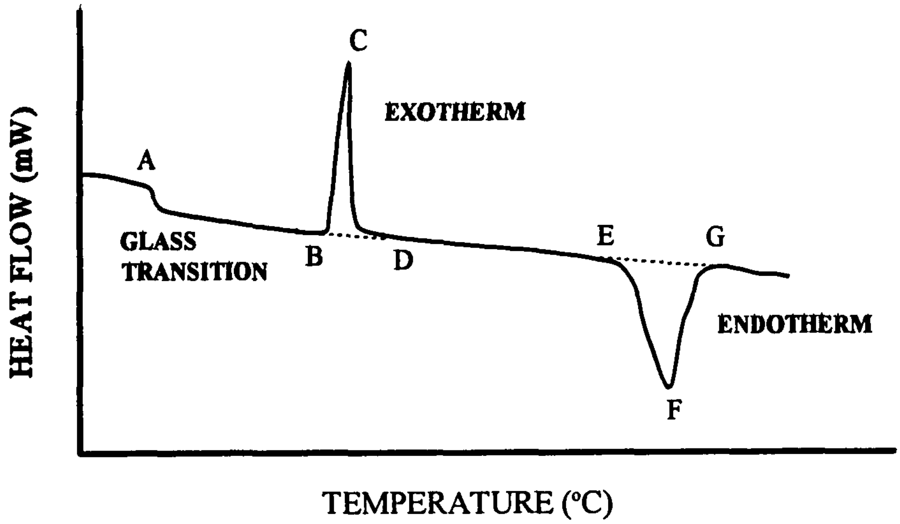


Figure 4.6: A typical non-isothermal DSC scan for a semi-crystalline polymer. Point A represents the glass transition (indicated by a change in the specific heat), C represents an exothermic transition (e.g., crystallization) and F represents an endothermic tranisition (e.g., melting). Areas BCD and EFG are indicative of the transition enthalpy

liquid nitrogen cooling prevented the use of high quenching rates and as a result some crystallization was possibly lost in the cooling segment. Specifically the following program was used to analyze the samples:

- Equilibrate at 150°C
- Ramp at 10°C/min to 300°C
- Isothermal for 5 min
- Ramp at 200°C/min to T_c (required isothermal temperature)
- Isothermal for 60 min

The run could be terminated when the crystallization process was over. The initial heating run was used to determine the T_m from the previous isothermal run. Due to the very high crystallization rates of nylon 6,6, it is only possible to conduct isothermal experiments in a narrow temperature range (220-235°C). The crystallization rate becomes too fast around 220°C (Figure 4.7) and too slow around 235°C (Figure 4.8) for accurate measurement by the DSC. There is some subjectivity in determining the onset and the end point of the crystallization process. The total time for crystallization is measured as the difference between the onset and end of the crystallization exotherm (Figures 4.7 and 4.8) and this is plotted against the isothermal crystallization temperature. The temperature range of measurement is obviously different for the various blends, due to the changes in thermal behavior.

In the quenching experiments, the blend sample was heated to 300°C and removed from the DSC cell and quickly immersed in ice water. It was hoped that the rapid quenching could prevent crystallization from taking place and lead to an amorphous sample. The cold crystallization exotherm was examined in the subsequent heating run. The peak temperature

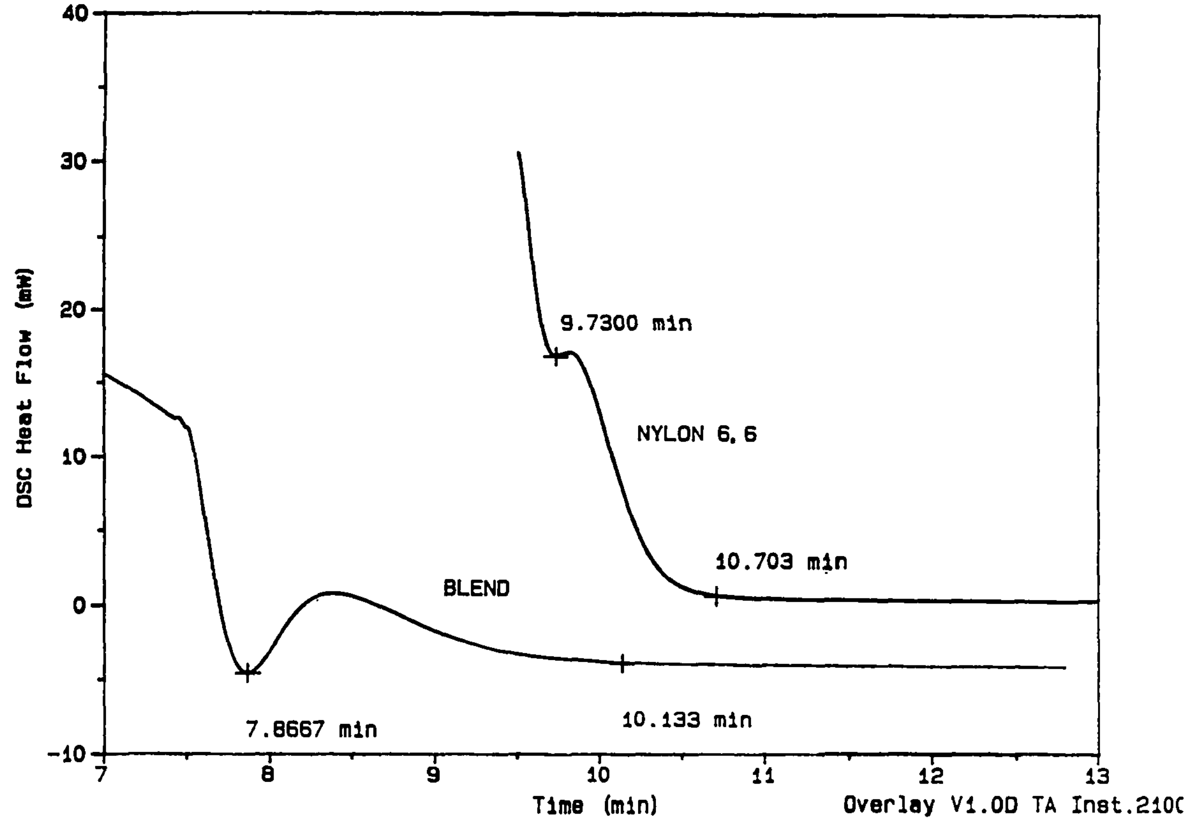


Figure 4.7: Isothermal crystallization of nylon 6,6 and Zytel 101/Zytel 330 blend at 223°C

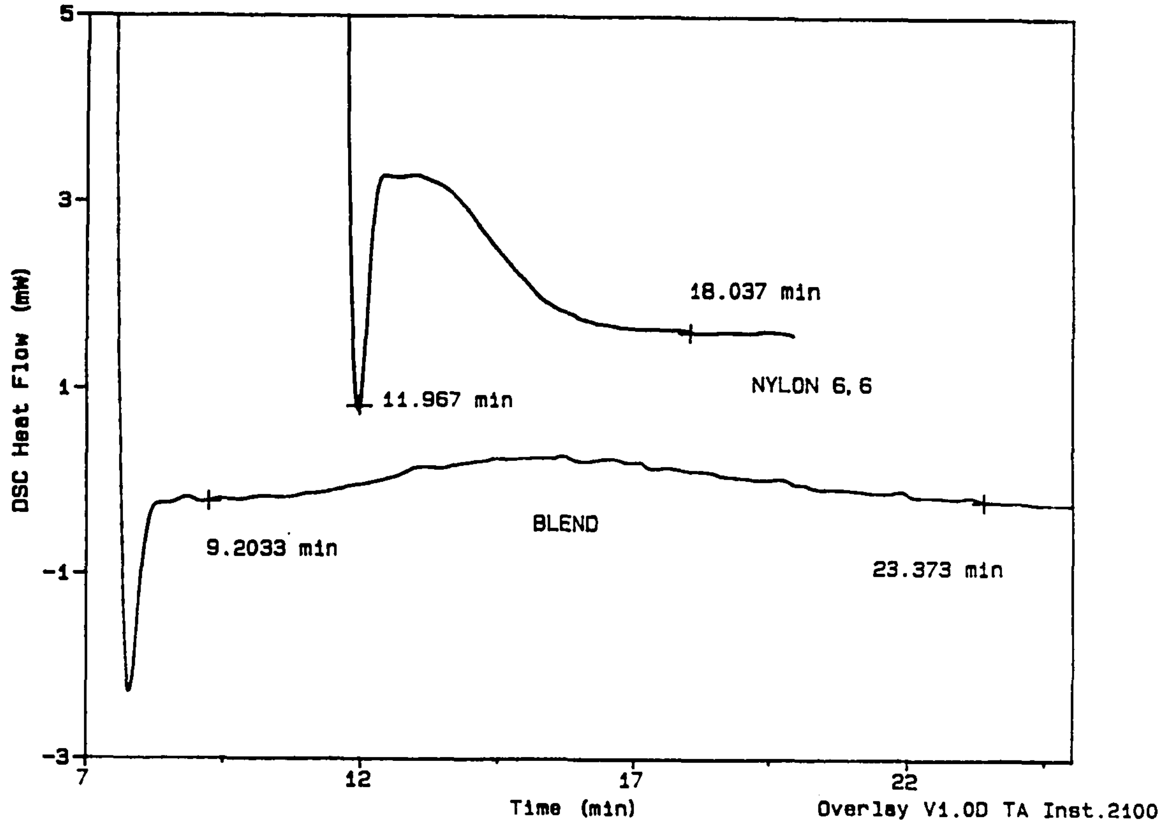


Figure 4.8: Isothermal crystallization of nylon 6,6 and Zytel 101/Zytel 330 blend at 235°C

value and the area of the cold crystallization exotherm gives information about the crystallization rates encountered during the quenching experiment.

All runs were carried out in standard aluminum crimped pans. A nitrogen purge was run at all times to prevent oxidation of the samples. High purity (99.9999%) nitrogen was substituted for the standard nitrogen, especially in the runs involving annealing in the melt. This was to ensure minimum oxidation of the sample.

Despite drying in the vacuum oven, it was found that residual solvent remained in the solution blended samples, and influenced the thermograms, especially in the case of m-cresol. This residual solvent had to be removed, and this was done by heating the sample in an open pan in the DSC itself. A typical solvent (m-cresol here) removal run is shown in Figure 4.9. Before carrying out the run, the sample was heated to a temperature above the solvent boiling point and held isothermally for 2-3 minutes. This proved to be adequate and resulted in a weight loss that was taken into account in the subsequent runs. No weight loss was observed in the subsequent runs confirming complete solvent removal. The standard runs were conducted in a crimped pan using nitrogen purge.

Hoffman-Weeks Plot: The melting point is a function of the temperature at which the material has been crystallized. In this method, the material is crystallized isothermally at different temperatures (T_c) and the melting point of that material noted in the subsequent run (T_m). The equilibrium melting point (T_m°) is determined by plotting the melting temperature versus the corresponding isothermal crystallization temperature and extrapolating the data to $T_m=T_c$. A typical plot is shown in Figure 4.10 [39], for the case of polyphenylene sulfide substituted with different levels of meta phenylene. Following the change of T_m° as a function

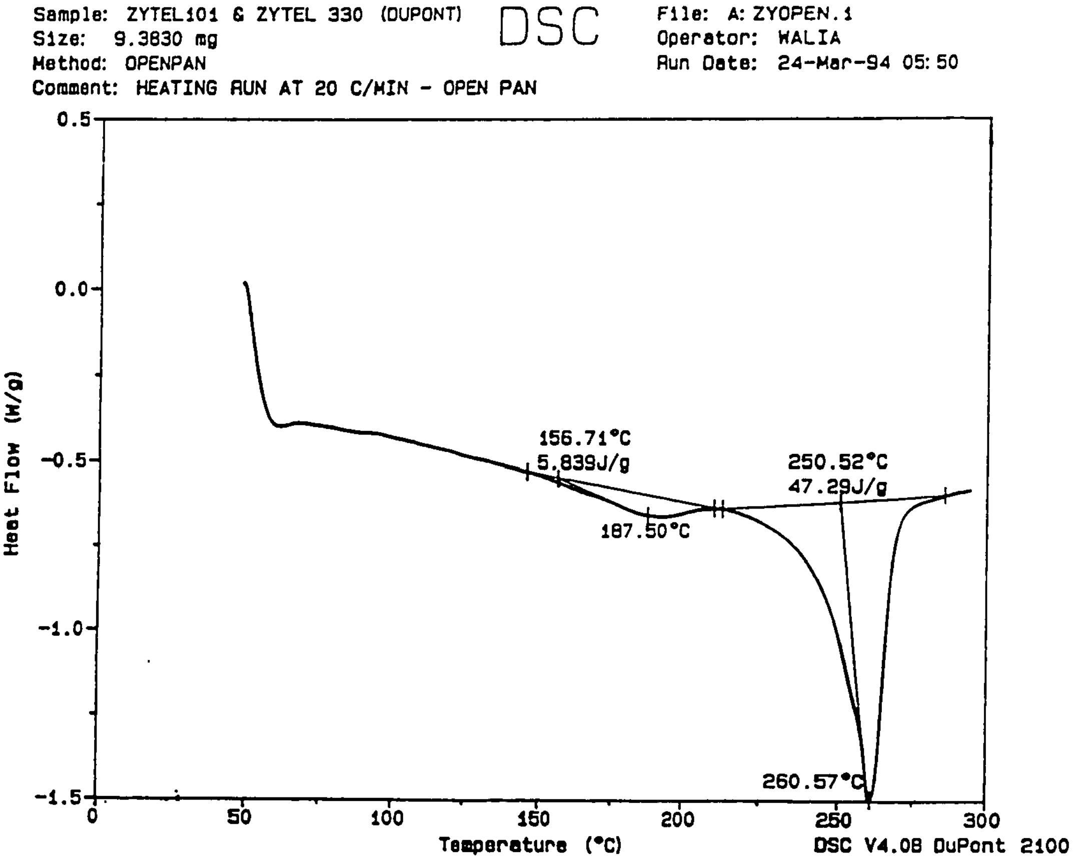


Figure 4.9: A typical open pan run with solvent removal (Zytel 101/Zytel 330 blend)

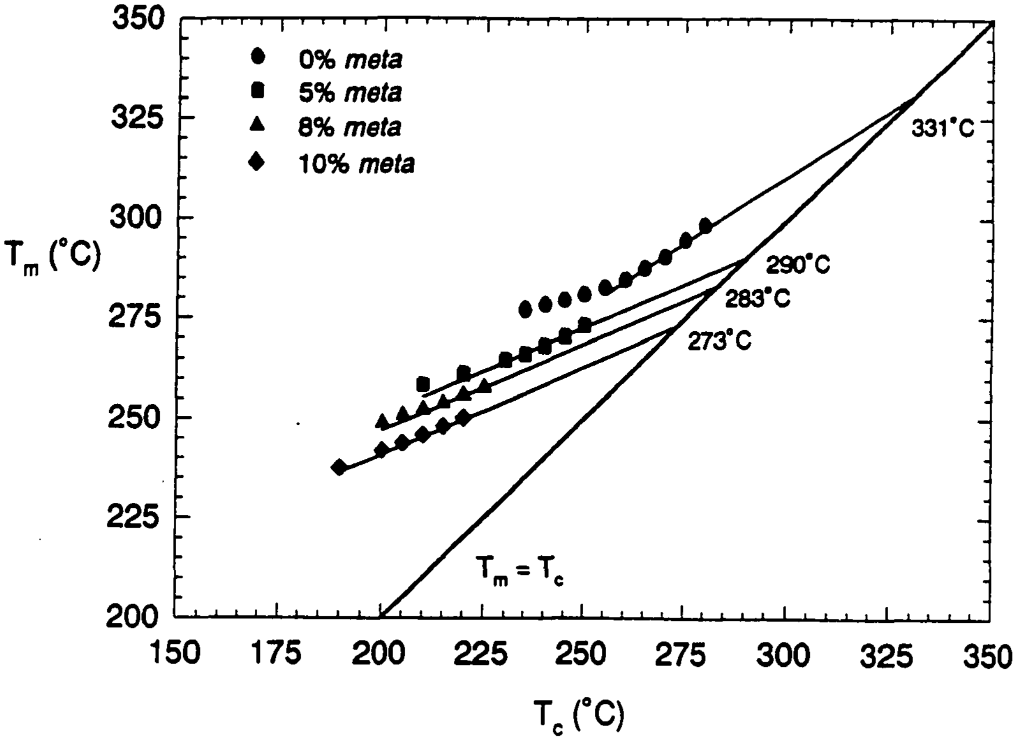


Figure 4.10: A typical Hoffman-Weeks plot for polyphenylene sulfide substituted with different levels of meta phenylene (from ref. 39)

of the annealing time will give a quantitative indication of the extent of reaction. As discussed earlier, as the transamidation reaction proceeds, block copolymers with smaller block lengths are formed, and eventually a true random copolymer results. The $T_m°$ decreases as the block length decreases with the random copolymer having the least $T_m°$. The melting point of the random copolymer can be estimated by the following expression, given by Flory [40]:

$$\frac{1}{T_m} - \frac{1}{T_m^A} = (-\frac{R}{H_\mu})\ln X_A \qquad \ldots (4)$$

where T_m = *Copolymer melting point*
T_m^A = *Homopolymer melting point*
H_μ = *Latent heat of fusion of homopolymer repeat unit*
X_A = *Mole fraction of major component A*
R = *Molar gas constant.*

Knowing the initial weight fractions and the molecular weights of the components, X_A can be calculated. H_μ, latent heat of fusion of nylon 6,6, is known. Hence, the melting point of the random copolymer can be calculated.

4.6 Dynamic Mechanical Thermal Analyzer

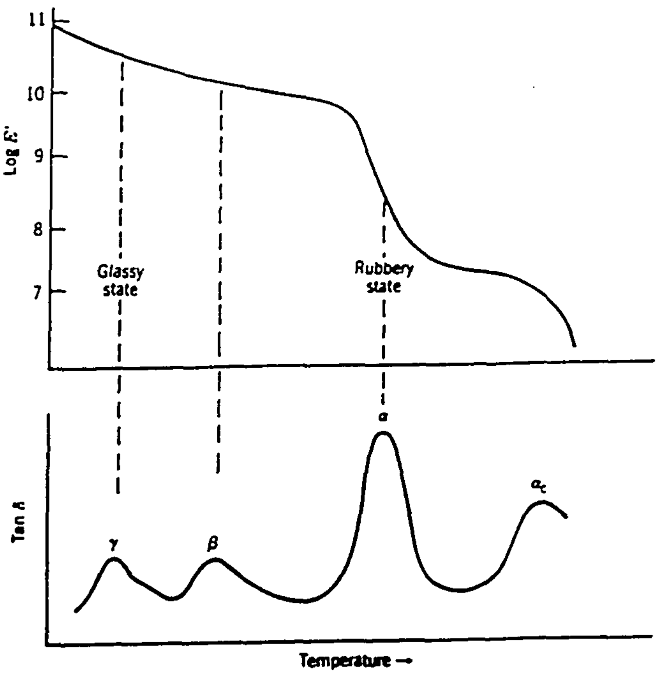
Dynamic properties are properties of materials when deformed under periodic forces (sinusoidal). In the case of viscoelastic materials (such as polymers), the resulting deformation varies sinusoidally with time too, but with a phase lag. This enables the determination of dynamic moduli such as storage modulus, loss modulus and the mechanical damping or internal friction. The storage modulus reflects the inherent stiffness of the material under dynamic loading conditions and indicates the amount of energy stored by the sample. The loss modulus gives the amount of energy dissipated as heat during the experiment. Polymers are examples of viscoelastic materials which, as the name suggests, have properties of both viscous liquids and elastic solids. Elastic materials have the ability to store mechanical energy without any dissipation of energy while viscous materials have the ability to dissipate the energy completely (with no storage).

A typical DMTA plot of an amorphous material is shown in Figure 4.11 [41], as a function of temperature. In the region where the dynamic modulus - temperature curve has an inflection point, the tan δ curve goes through a maximum. The dynamic modulus changes from roughly 10^{11} dynes/cm^2 in the glassy state to about 10^7 dynes/cm^2 in the soft rubbery state. Hence the tan δ vs. temperature gives an accurate and very sensitive measurement of the glass temperature T_g.

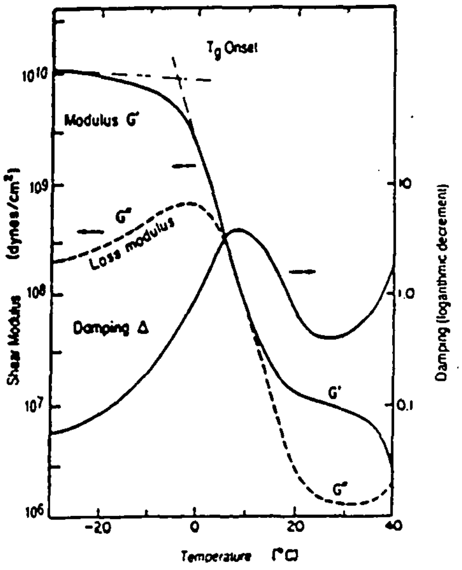
A Polymer Laboratories DMTA, donated by IBM, was used. It is equipped with only one fixture, requiring thin films (100-200 μm approximately). A preset force is applied to the sample in a tensile mode and this force is maintained at a steady level. The DMTA then applies a sinusoidally varying force to the sample to achieve a given peak strain value. The sample storage modulus, loss modulus, damping, tan delta, are then calculated.

Procedure: A typical run would involve the following. Sample preparation and accurate measurement of the sample dimensions - length (between the clamps), width and thickness. These have to be input to the instrument. The constant force needs to be determined from the dimensions and the elastic modulus of the sample (typically 0.65-0.90 N). The software is programmed to normally go from room temperature to about 20°C above the expected T_g at 5°C/min. This can be changed for improving the resolution in the consecutive runs, if needed.

Sample preparation: It is difficult to prepare uniform film samples for nylon 6,6 with



Typical dynamic mechanical properties of polymer.



Typical dynamic mechanical behavior for viscoelastic functions, G', G", and log decrement (isochronal plot) log decrement = tanδ ; data taken at 1 Hz.

Figure 4.11: Typical DMTA Plot of an Amorphous Material (from ref. 41)

thicknesses in the range of 100-200 µm. After considerable trials, the following hot press procedure was developed. A thick continuous piece of extruded filament is selected and placed between two smooth metal plates. The plates were then placed on top of a hot plate. The plates are covered with aluminum foil which prevents the sample from sticking to the plate and helps in peeling the prepared sample. The foil should be very uniformly covered on the plate, else it will distort the surface finish of the sample. The temperature of the hot plate was calibrated so that the temperature between the plates is sufficient to melt the sample. It takes upto 1 min for the sample to start melting. Once the sample starts to melt, pressure is applied for 1 min on the plates by means of weights and by physically pressing the upper plate down. The plates are then removed from the hot plate and allowed to cool down. The pressed sample is removed by peeling it off the aluminum foil. The thickness is checked with a screw gauge and the above procedure repeated until the desired thickness is obtained. Generally 2-3 pressings are sufficient. A sample of desired length and width was cut from this piece. The thickness was checked at different points (10-15 points) and an average thickness was used (the point to point variation in thickness was roughly 10 µm).

4.7 Rheometrics Mechanical Spectrometer (RMS-800)

This instrument is classified as a mechanical spectrometer and is used as a mechanical test system for evaluating viscoelastic properties of polymeric materials, especially melts. The polymer sample is in the form of a disc that is placed between two circular parallel plates. The instrument can be operated in either dynamic or steady state. In dynamic mechanical analysis of the test sample, the instrument applies a precise sinusoidal shearing (strain) to the test sample and accurately measures the sample's response. Microprocessor analysis of the applied strain and resulting response yields the sample's elastic modulus (G'), viscous modulus (G''), and loss modulus (tan δ).

These tests conducted for the pure material and the blends, would give miscibility information in the melt phase, complimentary to the DMTA data, which gives information in the solid phase.

Sample Preparation: Samples in the shape of discs of thickness 1.5-2.5 mm are needed. The procedure to prepare the initial films was the same as for the case of the DMTA. Spacers of the required thickness were placed on the plates to prepare the films. Several filaments or pellets need to be used to prepare the films. The thickness is checked with a screw gauge and the pressing procedure repeated until a uniform sample is formed. Then a disc (less than 25 mm diameter) is cut from this sample. To load the sample onto the instrument the following procedure is followed. The disc is placed in the center of the bottom plate and the top plate is slowly brought down until it is slightly above the sample. The oven is closed and the temperature is set at 300°C. After the set temperature is reached, 5 mins are allowed for the sample to equilibrate at that temperature. Then the top plate is brought down until it just touches the sample; indicated by a deflection in the normal force indicator. At this point the sample is allowed to melt completely. Once that has been achieved, the plate is lowered and the sample slowly compressed (the normal force should not exceed the safe limits). The compression should be continued until the sample completely fills the space between the plates. A low shear rate should be used to distribute the sample evenly between the plates. After the sample has been filled properly between the plates, the gap between the plates is noted and used for the instrument setting.

Cleaning: At the end of the run, the plates are separated at the operating temperature (normally 300°C), when the sample is in the molten state. This is to prevent the development of any stresses due to the solidification of the sample. The separated plates are cooled to 200°C in the furnace. Once that temperature is reached, the furnace is opened and the plates are cleaned with adipic acid to remove the sample from the plates. Since the plates cool very rapidly, the furnace has to be closed and reheated to 200°C to conduct further cleaning. The plates can be cleaned to a great extent by this procedure. Additional cleaning can be carried out mechanically or by using formic acid (degraded material does not dissolve and has to be mechanically removed).

Both steady shear and dynamic runs were made on the pure material and the blends. In the steady mode, the test sample is placed in rotational shear at a given shear rate and the resulting shear stresses are measured by the instrument transducer. The logarithmic rate sweep test mode is utilized in which an initial and final rate (in 1/s) is input and the number of points per decade chosen. The torque and shear viscosity are followed as a function of shear rate. In the dynamic mode, an oscillatory strain is applied to the sample and the instrument measures the resulting stress. A frequency sweep (logarithmic mode) is conducted in which the upper and lower frequency limits are entered (in radians/second) and upto 10 measurement points per decade can be selected. The strain should be in the linear viscoelastic range of the material. The material functions - G', G" and η' are followed as a function of frequency. A low strain of 10% was used for these experiments. All steady and dynamic runs were conducted at 300°C. This temperature had already been reached during sample loading and no initial equilibration or waiting period is needed.

4.8 Optical Microscopy

A Zeiss Axioscop 451485 optical microscope equipped with Lekam THMS 600 hot-stage and TMS92 temperature controller, was available. The hot stage can be purged with an inert gas. The isothermal crystallization (spherulitic growth) can be followed by a method similar to that used in the DSC. The sample is heated above the melting point and held there for around 5 mins to destroy all existing spherulites. Then the sample is quenched to the desired crystallization temperature and held isothermal until the crystallization process is over. The growth of the spherulites is followed visually as a function of time. This is complimentary to the DSC isothermal data since it also reveals the size and shape of the spherulites. It is a more direct proof of any possible retardation in crystallization.

The thickness of the sample is critical in observing spherulites under crossed polarizers. The film has to be thinner than 50μm for successful viewing of birefringence. Thin film samples were prepared by placing a small amount of material between glass and cover slides. These were placed on a hot plate preheated to obtain melting temperatures. Weights were placed on top of the cover slide to squeeze the material. Spacers were placed between the glass and cover slides to obtain the desired thickness. Thin samples can be successfully prepared in this manner. However, the effect of pressure and time has to be properly understood in order to prepare samples on a consistent basis. Another advantage of this method is that the prepared sample can be directly used in the hot-stage, without any additional work.

CHAPTER 5

ADDITIVE SCREENING EXPERIMENTS

This chapter summarizes the work that was carried out in the first stage of this dissertation. A number of polymeric additives, both amorphous and semi-crystalline, were evaluated. Different approaches were used in the selection of the additives. These are outlined below:

1) Amorphous polymers: As discussed earlier (Chapter 2), an amorphous additive miscible with nylon 6,6 and having a higher T_g would produce the following effects:

- enhancement of blend T_g
- slight depression of the equilibrium T_m
- slower polymer diffusion (and hence slower spherulitic growth rate)
- no expected change in total level of crystallinity

Based on this approach, the following additives were selected, with increasing T_g values:

Nylons:

Trogamid-T (T_g=125°C)

Zytel 330 (T_g=153°C)

Non-nylons:

Polyacrylic acid (T_g=118°C)

Polycarbonate (T_g=150°C)

Polyphenylene oxide (T_g=213°C)

2) Semi-crystalline polymers: Polymers that could possibly interact with nylon 6,6 were investigated. The interaction could be in terms of the disruption of the hydrogen bonding or an effect on the crystallization growth process. There was a possibility of co-crystallization of the two polymers. In this case, selection of an additive with a lower T_m (or lower T_c) could lead to the blend crystallizing at a lower common T_c. Hence, polymers with a range of low T_m's were selected:

Nylons:

Nylon 6 (T_m=223°C)

Nylon 6,12 (T_m=216°C)

Nylon 12 (T_m=183°C)

Non-nylons:

Exxelor PO 1015 (T_m=143°C)

3) Reactive polymers: The final approach was to look at polymers that could chemically react with nylon 6,6. Some of the possible reactions were described in Chapter 2. Polymers such as polymethylmethacrylate, polyacrylamide (Separan AP30), polyacrylic acid, polystyrene sulfonate, Exxelor PO 1015 (maleic anhydride), Hypermer FP4 (contains anionic polyester) and various types of nylons were selected on this basis.

Table 5.1 shows the complete list of additives tried, the source of the additives, the method of blending and the level of concentrations tried. The results are discussed for each additive and are summarized in Table 5.4 at the end of the chapter.

TABLE 5.1: LIST OF ADDITIVES TRIED

	ADDITIVE	BLENDING PROCEDURE[a]	ADDITIVE LEVELS (wt/wt%)	SOURCE OF ADDITIVE
1.	Nylon 6(3), T Poly (trimethyl hexamethylene terephthalamide)	Solution[b] (mc[c])	15, 20	Scientific Polymer Products
2.	Nylon 6, 12	Solution[b] (mc) Melt[a]	15, 25 25	Scientific Polymer Products
3.	Zytel 330	Solution (mc) Melt	10, 20 10, 20, 25	Dupont
4.	Trogamid-T®	Solution (mc) Melt	10, 20 10, 20, 25	Huls America
5.	Polyethylene Glycol (Carbowax® PEG 20 M)	Solution[d] (fa[e])	15	Union Carbide Chemicals & Plastics Company, Inc.
6.	Polyacrylic Acid (M.W. 450,000)	Solution[d] (fa)	15	Polysciences
7.	Polyethylene Oxide	Solution[d] (fa) Melt	15 25	Polysciences
8.	Polystyrene Sulfonate (M.W. 70,000)	Solution [d] [f]	15	Scientific Polymer Products
9.	Separan AP30® Polyacrylamide	Solution[d] (fa)	15	Dowell R & D
10.	Nylon 6	Solution[d] (fa)	15	Scientific Polymer Products
11.	Polymethylmethacrylate (PMMA)	Solution[d] (fa) Melt	15 25	Polysciences
12.	Nylon 12	Melt	25	Scientific Polymer Products
13.	Polycarbonate (BHPP 801)	Melt	25	GE Plastics

[a] All melt blending work was carried out with nylon 6,6 from Dupont (Zytel 101)

[b] Solution blending using SPP nylon 6,6

[c] mc=meta-crescol

[d] Solution blending using Rhodia nylon 6,6

[e] fa=formic acid

[f] Polystyrene sulfonate solution in water was mixed with nylon 6,6 solution in formic acid and the resulting precipitate dried

TABLE 5.1: LIST OF ADDITIVES TRIED

14.	Polyphenylene Ether (BHPP 820)	Melt	25	GE Plastics
15.	Exxelor PO1015 (Maleic anhydride)	Melt	25	Exxon Chemicals
16.	Hypermer FP4 (contains anionic polyester)	Melt	25	ICI Americas, Inc.
17.	Silicone Oil	Melt	25	Fisher Scientific

5.1 Different Nylon 6,6 Polymers

Three different nylon 6,6 resins were used in this work. Early work with solution blending utilized the polymer from Scientific Polymer Products (SPP). The footnotes in Table 5.1 indicate which nylon 6,6 was used to prepare each type of blend. Some solution blending and all the melt blending was carried out with DuPont's Zytel 101. This was preferred for melt blending since it was easier to extrude on the Maxwell extruder as compared with Rhodia's nylon 6,6. All work in the second stage was carried out with the Rhodia nylon 6,6. Published reports [42] place the weight average molecular weight of Zytel 101 at 15,000. Rhodia's nylon 6,6 supposedly had a similar molecular weight. It was used for all the solution blending work after it was received. Figure A.1[8] shows the DSC thermograms for the different types of nylon 6,6. The crystallization and melting behavior of the three types of nylon 6,6 are similar. Hence, there should not be any variability in the different types of blends as a result of the type of nylon 6,6 used to prepare the blend The melting point (peak value) is roughly 263°C and the crystallization temperature T_c (peak value) is 236°C. Unless otherwise stated,

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[8] All DSC runs are reported in Appendix A

the melting and crystallization points are always taken to be the peak values.

Shown in Figure A.2 is a thermogram of Zytel 101 after being processed through the Maxwell extruder. There is no noticeable change in the thermal behavior, as compared with the unextruded pellets. Note that repeated runs on the same sample were found to yield essentially identical results confirming that nylon 6,6 does not undergo changes in melting and crystallization behavior due to thermal treatment. Annealing in the melt at 300°C for a period of 4 hrs did not produce any significant change in the thermal behavior. This is relevant since later results will show that most of the blends undergo significant changes on thermal treatment.

5.2 Melt Blend Uniformity

It was essential to confirm that the Maxwell extruder gave blend samples whose composition matched the overall composition of the mixture fed to the extruder and that there was no sample-to-sample variations. For miscible blends, the glass transition temperature is easily related to the individual T_g's and composition. In our case, though, it was very difficult to determine the T_g of nylon 6,6 and its blends using the DSC technique. As a consequence, it was decided to blend nylon 6,6 (Zytel 101, Dupont) with another semi-crystalline polymer, nylon 12, having very different T_m and T_c values. Compositions could then be determined with the help of heats of fusion and crystallization values. Shown in Figure A.3 is a thermogram of pure nylon 12 while Figures A.4-A.7 display results for four different samples of a 75/25% wt/wt blend of nylon 6,6 and nylon 12 (SPP). The samples were taken from different portions of the extruded strand. The heats of fusion, corresponding to the pure components, nylon 6,6 and nylon 12, for the different samples are closely matched (Table 5.2). Pure nylon 6,6 has ΔH_f=63.5 J/g while pure nylon 12 has ΔH_f=57.3 J/g. It is clear that the four different samples have the same composition.

Table 5.2: Heat of fusion values (ΔH_f) for nylon 6,6 and nylon 12 from different portions of the extruded strand from the Maxwell extruder

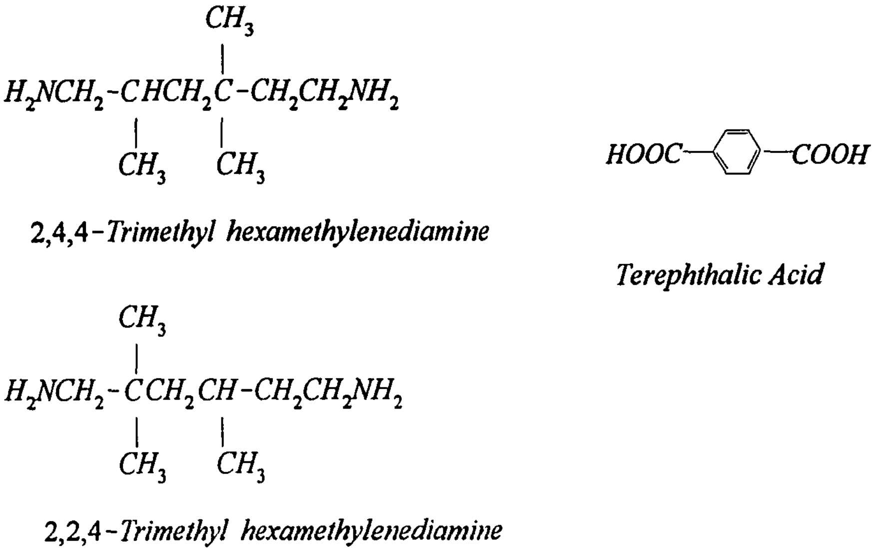
Sample No	ΔH_f (nylon 6,6 peak) (J/g)	ΔH_f (nylon 12 peak) (J/g)
1	42.15	17.11
2	41.77	16.16
3	42.97	16.61
4	42.69	16.25
Mean	42.40	16.53

5.3 Results with Amorphous Polymers

If an amorphous polymer is used to form a blend with nylon 6,6, crystallization in the blend would require the exclusion of the amorphous additive, and this diffusion process would slow down the crystal growth rate. Furthermore, the additive would act as a diluent and depress the equilibrium melting point. Simultaneously, if the additive T_g is higher than that of nylon 6,6, the blend T_g would lie between that of the two constituents and would be higher than the nylon 6,6 value. Consequently, as a result of blending, (T_m-T_g) would become smaller than that for pure nylon 6,6. Since crystallization takes place only in a range of temperatures bounded by T_m and T_g, at the same cooling rate, therefore, the time available for crystals to grow would be less in the blend than in the nylon 6,6 melt. Next, the effect of adding different amorphous polymers to nylon 6,6 is discussed in detail.

5.3.1 Blends with Amorphous Nylons

Two different amorphous nylons were tried. These were Zytel 330 from DuPont and Trogamid-T from Huls America. Trogamid-T is made from terephthalic acid and a 1:1 mixture of 2,4,4 Trimethyl hexamethylene-1,6-diamine and 2,2,4 Trimethyl hexamethylene-1,6-diamine; its structure has been published [43] and the monomers are shown in Figure 5.1. Zytel 330 is reportedly a mixture of 70% nylon 6T and 30% nylon 6I [43]. Its structure is shown in Figure 5.2. Thermograms of the two polymers are shown in Figures A.8 and A.9; measured T_g's were 125 °C for Zytel 330 and 153 °C for Trogamid-T.



$$H_2NCH_2\text{-}\underset{CH_3}{C}HCH_2\overset{CH_3}{\underset{CH_3}{C}}\text{-}CH_2CH_2NH_2$$

2,4,4-*Trimethyl hexamethylenediamine*

$$H_2NCH_2\text{-}\overset{CH_3}{\underset{CH_3}{C}}CH_2\underset{CH_3}{C}H\text{-}CH_2CH_2NH_2$$

2,2,4-*Trimethyl hexamethylenediamine*

Terephthalic Acid

Figure 5.1: Chemical structure of Trogamid-T monomers

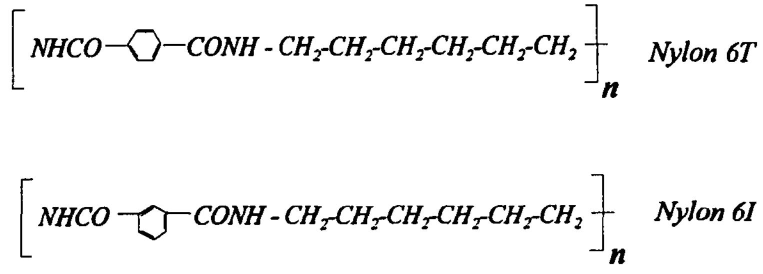


Figure 5.2 Chemical structure of Zytel 330

An unusual aspect of all the results obtained as part of this blending study was the lack of any observed significant effect of the added polymer on the crystallization behavior of nylon 6,6, during a normal DSC heating and cooling run. This was extremely disappointing until it was discovered that in most cases, repeated runs in the DSC caused the thermograms to change with blend T_c's moving significantly to lower temperatures. As a consequence, it was decided to anneal the blend samples in the DSC at 300°C for varying periods of time. The melt annealing produced significant changes in the melting and crystallization behavior of the blends.

Shown in Figures A.10-A.13 are results for a 10% solution blended sample of Zytel 101 and Trogamid-T. Note that the T_c for melt processed Zytel 101 is approximately 236°C (see Figure A.2). The addition of the amorphous nylon is effective in reducing T_c slightly to 227°C. Annealing the sample at 300°C for a total of 90 minutes progressively lowers the T_c to 211°C, 203°C and 183°C, at the end of each 30 minute period. Note that T_m is also lowered to 261.6, 255.7, 249.0, and 238.3°C respectively. The heat of fusion values (ΔH_f)

are reduced to 65.7, 60.3, 52.0 and 45.1 J/g respectively.

Similar results were obtained with the other amorphous polyamide (Zytel 330) blends. Figures A.14 and A.15 show the thermograms for a 15% solution blend of nylon 6,6/Zytel 330 annealed for 60 and 105 mins. The corresponding T_c's are 208 and 194°C, respectively.

Since initial data were obtained at different solution blend and melt blend compositions and for different annealing times, it was difficult to say whether solution blending was more effective than melt blending and whether Zytel 330 was preferable to Trogamid-T. A comparative study was undertaken wherein data were obtained on both melt (Maxwell extruder) and solution blended samples at 10 and 20% additive concentration at annealing times of up to two hours; the nylon 6,6 utilized was Zytel 101. Results are summarized in Table 5.3. Although there are minor, inexplicable, internal inconsistencies in the numbers shown in Table 5.3, in general solution blending appeared to give better results, except for the 10% Zytel 330 solution blend. However, the overall trend is that blending with an amorphous nylon is effective in reducing the rate of crystallization. Trogamid-T appears to be more effective than Zytel 330 and solution blending appears to give better results. The last conclusion is understandable inasmuch as solution blending yields mixing on a molecular level while melt blending does not. A further observation of interest is that while Zytel 330 dissolves easily at room temperature in formic acid, Trogamid-T does not. Thus, it was necessary to heat the mixture of Trogamid-T and formic acid in a sealed bottle to promote solubility. This high temperature treatment may have led to the solution blended Trogamid-T being more reactive as compared to Zytel 330.

Finally, it is speculated that holding the sample at an elevated temperature for an

TABLE 5.3: Effect of Annealing Time on T_c(°C) of Trogamid-T and Zytel 330 Blends

	Initial Value	30 min	60 min	90 min	120 min
10% Trogamid-T solution blend	227	211	203	183	
10% Zytel 330 solution blend	236	233	232	230	
20% Trogamid-T solution blend	225	220	205	175	
20% Zytel 330 solution blend	232	228	213	174	
10% Trogamid-T melt blend	221	214	213	213	211
10% Zytel 330 melt blend	232	229	227	223	218
20% Trogamid-T melt blend	231	227	226	225	
20% Zytel 330 melt blend	236	231	226	222	217

extended period of time is leading to interchange reactions between the components resulting in copolymerization. While transamidation and transesterification occur frequently, as discussed earlier, whether these two nylons were reacting with each other could only be determined by additional research. Also note that annealing nylon 6,6 alone did not result in altered crystallization behavior.

In an effort to prove that adding amorphous nylon to nylon 6,6 does, indeed, retard crystallization, isothermal crystallization experiments were done in the DSC. Here the blend and pure nylon 6,6 samples were rapidly cooled from the melt to a temperature between T_g and T_m and held there isothermally and the course of crystallization followed. The total time for crystallization is taken as the difference between the beginning and end of the crystallization exotherm. The results are plotted in Figure A.16 as the total time for crystallization versus the crystallization temperature. At the temperatures at which data could be obtained, it appeared that adding 20% Zytel 330 to Zytel 101 cut the rate of crystallization by a factor of two. Since these samples were not subjected to melt annealing, it is suspected that further changes would be obtained if an annealing step were to be introduced.

It needs to be mentioned that increasing the DSC cooling rate from 5 to 40°C/min lowered the T_c and the rate of crystallization of pure nylon 6,6 and also its blends with amorphous nylon. Figures A.17-A.19 show the effect of cooling rate on T_c of pure nylon 6,6 and a 20% nylon 6,6/Zytel 330 blend at 5, 20 and 40°C/min. It was found that T_c decreases progressively with increasing cooling rate, both for the pure component and the blend. This is to be expected since at the higher cooling rate there is less time for the material to crystallize and hence complete crystallization takes place at a lower temperature. However, the blend T_c is always lower than that of pure nylon 6,6, suggesting a lower crystallization rate. The blend exotherms were always broader than the pure component, indicating slower crystallization rates. There was, however, no significant influence of the cooling rate on the total crystallinity developed in the sample.

Since in a polymer processing operation, the molten polymer is often rapidly quenched, to compare crystallinity developed under these conditions, quenching experiments need to be performed. In such an experiment, the molten samples are removed from the DSC and immediately introduced into ice water. The quenched samples are then heated at a rate of 60°C/min in the DSC. Figures A.20 and A.21 show the DSC runs for the quenched pure material sample and the blend, respectively. There is significant recrystallization (cold-crystallization) during the heating run, for both types of samples, indicating suppression of crystallization during the quenching process. Cold-crystallization occurs when the crystallization rate is too slow to allow complete crystallization at high cooling rates from the melt (e.g., during quenching).

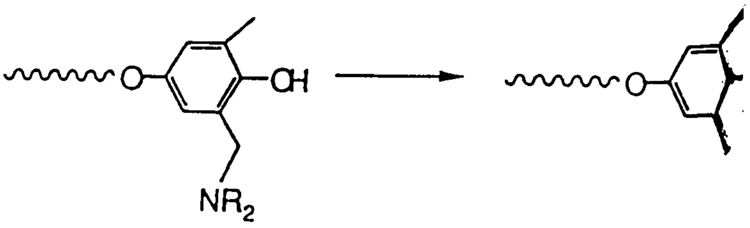
The recrystallization peak temperature is 74.6°C for pure nylon 6,6 and 95.9°C for the blend (21°C higher), showing that the process of crystallization is slower for the blend. Based on the heat of fusion values, it appears that the quenched nylon 6,6 sample developed 26% crystallinity during recrystallization whereas the blend developed 23% crystallinity (corrected for the weight percentage of nylon 6,6). Thus there is a 3% reduction in crystallinity as a result of blending or equivalently 10% less spherulites. The quenching experiments support the conclusions drawn from both the non-isothermal and isothermal data, revealing actual reductions in crystallinity that can be obtained in a polymer processing operation as a result of lowered crystallization rates.

5.3.2 Blends with Other Amorphous Polymers

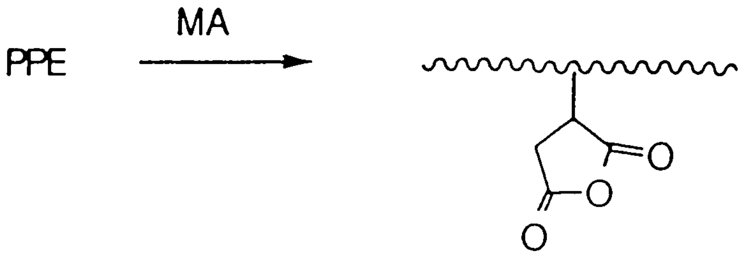
Three non-nylons were also blended with nylon 6,6 with different degrees of success. These were polyphenylene ether (BHPP 820, GE Plastics), polycarbonate (BHPP 801, GE Plastics) and polyacrylic acid (Scientific Polymer Products). The first two additives were melt blended while the last one could only be solution blended.

Blendex HPP 820 is commercial polymer used to increase the heat resistance of compatible polymers. It is amorphous and its T_g was measured to be 213°C (Figure A.22). It was mixed with Zytel 101 to give a blend containing 25% additive by weight. As in the case of amorphous nylons, the blend T_c decreased progressively on annealing at 300°C. After one hour, the T_c was 229°C and it went down to 218°C after another 45 minutes and finally to 200°C after a total annealing time of 2 hours and 30 minutes (Figures A.23-A.25). It is known [44] that unmodified blends of poly(phenylene oxide) and polyamide are brittle whereas materials which contain copolymer and impact modifier exhibit commercially useful properties. Maleic anhydride functionalization of poly (phenylene oxide) leads to the formation of graft copolymers whereas pre-functionalized resin leads to diblock copolymers, as illustrated in Figure 5.3 [44].

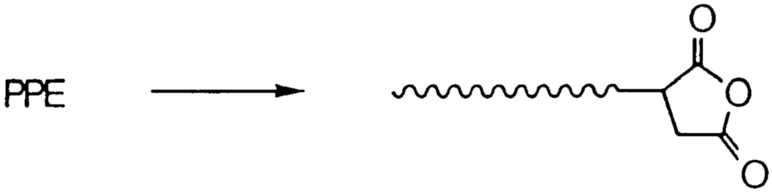
The T_g of Blendex HPP 801 polycarbonate was measured to be 150°C (Figure A.26). This was slightly more effective in lowering T_c as compared with polyphenylene ether when blended in the same proportion. After annealing for 45 minutes, the blend T_c was 222°C which fell to 217°C after another 45 minutes (Figures A.27 & A.28). Polycarbonate being a condensation polymer is expected to undergo interchange reactions, similar to the transamidation reactions, when subjected to high temperatures in the molten state. These



Scheme 1



Graft copolymer precursor (PPE-g-MA)



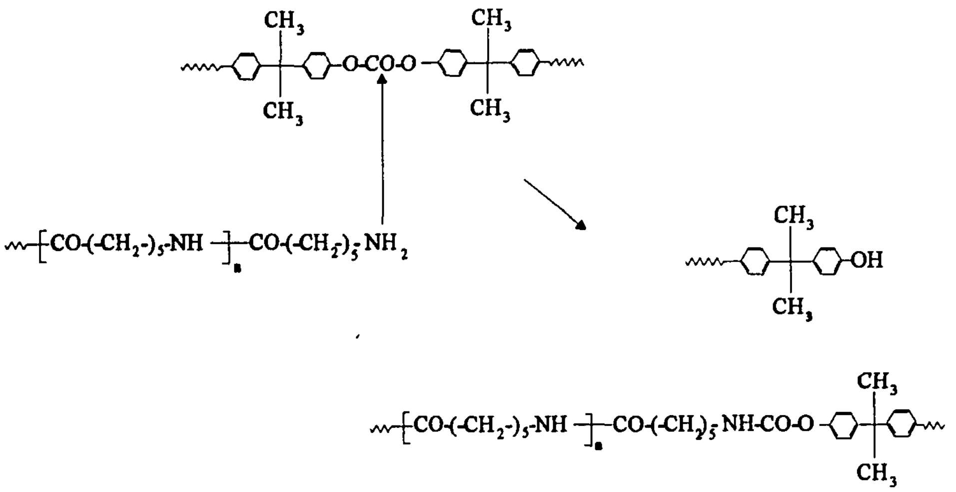
Diblock copolymer precursor (PPE-anhydride)

Scheme 2: Copolymer Structure

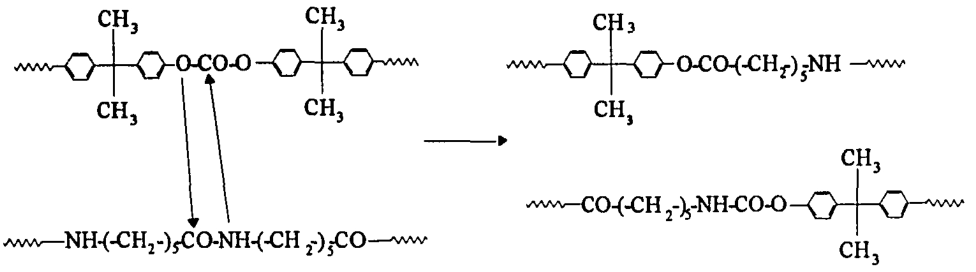
Figure 5.3: Reaction between polyamide and maleic anhydride functionalized poly(phenylene oxide); reproduced from ref. 44

reactions would give rise to block and random copolymers with urethane links. The urethane units should increase with the reaction time, indicating a reduction of the block size as a function of the extent of reaction. Blends containing polyamides and polycarbonates have received little attention. In contrast, interchange reactions have been extensively studied in the case of polyester/polyester and polyester/polycarbonate blends. Cortàzar et al. [45] studied a 50/50% wt/wt blend of nylon 6 and bisphenol A polycarbonate (PC). They observed a decrease in T_c and ΔH_c as a function of annealing time in the melt. They also observed two T_g's in the initial stages which tended to approach each other as the annealing time increased. When thermal treatment is maintained for 57 min or more, a single T_g is observed. Montaudo et al. [36] studied the nature of reactions occurring between nylon 6 and PC. Their results showed that only the cleavage of carbonate groups (Figure 5.4: Scheme 1), by means of nylon 6 amino end groups, is occurring at 240°C (similar reactions are known to occur in solution at room temperature). However, the exchange reaction between the inner amide groups and carbonate groups (Scheme 2) was significant only at 300°C.

Mixing with polyacrylic acid (PAA) is known to reduce the crystallinity in nylon 6 [46]. The polymer pair shows good miscibility with a single T_g being observed at all compositions. However the T_g - composition plots did not follow a monotonic function but yielded a maximum at PAA concentration of 25% wt. It was also observed that the melting point of nylon 6 was depressed substantially as PAA was blended upto 50% wt., and above this PAA content the nylon 6 component showed no tendency to crystallize in the cast films. It was suggested that specific interaction, such as hydrogen bond formation, between the amide groups of nylon 6 and the carboxyl groups of PAA is possible and could account for



Scheme 1



Scheme 2

Figure 5.4: Reaction between Nylon 6 and Polycarbonate Schemes 1 and 2 (taken from ref. 36)

the attainment of fairly good miscibility in the blends. In addition, acrylic acid containing copolymers are used [47] as reactive compatibilizers for toughening nylon 6. It was, therefore, considered likely that PAA would have the same effect on nylon 6,6. Unfortunately, this polymer cannot be melt extruded at 260°C. It was, therefore, dissolved in water and mixed with a solution of Rhodia's nylon 6,6 in formic acid. The molecular weight of PAA used was 450,000 and its measured T_g is 118°C (Figure A.29). Initially the blend, containing 15% wt/wt PAA, had a T_c that was the same as that of pure nylon 6,6 (Figure A.30). After annealing for 60 minutes, though, the blend T_c dropped dramatically to 179°C (Figure A.31).

In closing this section, it can be said that the use of either an amorphous nylon or polyacrylic acid would achieve the desired objectives. However, since PAA cannot be melt blended, one would have to seek out a chemically similar melt processable polymer.

5.4 Results with Semi-Crystalline Polymers

The logic of using semi-crystalline polymers which were miscible in the melt was that the rate of crystallization could conceivably be lowered if the two polymers could co-crystallize or influence each other's rate of crystallization by disrupting the hydrogen bonding or the molecular symmetry. In this quest, three different nylons and some non-nylons were tried. Some of the results were quite encouraging.

5.4.1 Blends with Semi-Crystalline Nylons

Nylon 6, nylon 12 and nylon 6,12 were obtained from Scientific Polymer Products. These nylons have different crystallization temperatures, lower than that of nylon 6,6. A thermogram of pure nylon 6 is shown in Figure A.32. Even though this polymer could be extruded by itself quite easily, blends with nylon 6,6 did not have a uniform composition (as compared to nylon 12). It appeared that there were differences in melt viscosity between the two polymers which would hinder proper mixing of the polymers. Consequently, solution blending was carried out using formic acid as the common solvent; additive amount was 16.4% by weight. The first DSC run (Figure A.33) showed two melting endotherms corresponding to the two constituent polymers. On crystallization from the melt, however, only a single T_c at 232°C was observed. Subsequently, the two melting peaks also merged to give a single peak close to the T_m of nylon 6,6. This suggests that co-crystallization was taking place. On annealing at 300°C, T_c decreased and the crystallization peak broadened. After 90 mins of annealing, T_c had decreased to 208°C (see Figure A.34).

As opposed to nylon 6 which could not be melt blended easily, nylon 12 could not be solution blended as it does not dissolve in formic acid. This polymer had a T_m of 181 °C and a T_c of 145 °C, and it was easily melt mixed with nylon 6,6 to give a blend containing 25% nylon 12. Initially the blend showed two melting peaks and two crystallization peaks roughly corresponding to the two pure components (see Figure A.4). There was an increase in T_c (158°C) of nylon 12 while the T_c of nylon 6,6 was practically the same (235°C). Surprisingly, there was a very small change in T_m of nylon 12 (175°C compared to 181°C for pure nylon 12), while the T_m of nylon 6,6 remained the same (235°C). This separate melting and crystallization behavior persisted even on annealing in the melt, and there appeared to be no signs of co-crystallization. That there was some interaction between the two nylons, though, was evident from the fact that the nylon 6,6 T_c value decreased progressively to about 201 °C after almost one hour of annealing (Figure A.35). There was also a significant change in the T_c value of nylon 12 (151°C compared with 181°C for the pure material).

A thermogram of nylon 6,12 is displayed in Figure A.36. For this polymer, T_m was 217°C and T_c was 184°C. It was melt and solution blended (using m-cresol) at a 25% level with nylon 6,6. There was strong interaction between the two polymers. The solution blended sample appeared to show co-crystallization and a reduction in the blend T_c to 199°C simply by heating and cooling the sample in the DSC three times without any significant high temperature annealing (Figures A.37-A.39). The melt blended sample, though, required much longer melt annealing to achieve the same effect; even so, it took 80 min to lower the T_c to 216°C (Figure A.40).

5.4.2 Blends with Other Semi-Crystalline Polymers

The only other semi-crystalline polymer that showed promise was Exxon's Exxelor PO 1015 which contains maleic anhydride and is used as a compatibilizer for olefinic polymers. This material had a T_m of 143°C and a T_c of 98°C (Figure A.41). A 75/25% nylon 6,6/PO 1015 melt blend took almost three hours of annealing to lower the T_c of nylon 6,6 to about 203°C (Figures A.42-A.44). During this time, the additive maintained its separate identity. This was obviously not as effective as some of the other additives discussed earlier.

Examination of the crystalline additives shows that nylon 6,12 was the most effective in reducing the T_c of nylon 6,6. It is also easy to melt blend and hence appears the most promising.

All the results discussed in this chapter are summarized in Table 5.4.

Table 5.4: Summary of Results

	ADDITIVE	CONCENTRATION (% wt/wt)	ANNEALING TIME AT 300 °C (min)	T_c VALUE (°C)
1.	Trogamid-T	10 (solution)	0	227
			30	211
			60	203
			90	183
2.	Zytel 330	15 (solution)	60	208
			105	194
		25 (melt)	0	232
			30	212
			50	180
2.	Blendex HPP 820 (PPE)	25 (melt)	60	229
			105	218
			150	200
3.	Blendex HPP 801 (PC)	25 (melt)	45	222
			90	217
4.	Polyacrylic Acid (PAA)	15 (solution)	0	235
			60	179
5.	Nylon 6	16.4 (solution)	0	232
			70	208
6.	Nylon 12	25 (melt)	0	235
			10	233
			25	225
			40	213
			60	201
7.	Nylon 6,12	25 (solution)	5	208
			10	203
			15	199
		25 (melt)	0	234
			60	221
			80	216
8.	Exxelor PO 1015	25 (melt)	90	224
			150	210
			170	204

5.5 Unsuccessful Additives

So far only additives that interacted with nylon 6,6 and showed promise for changing the thermal behavior have been considered. Of course, many other modifiers were tried - some for theoretical reasons and other because they happened to be easily available. These did not produce the desired effect for a variety of reasons. Some were simply not compatible with nylon 6,6 while others degraded in the extruder. These unsuccessful additives included:

- polymethyl methacrylate (PMMA)
- poly ethylene oxide (PEO)
- poly ethylene glycol (PEG)
- polyacrylamide (Separan AP 30)
- polystyrene sulfonate (PSS)
- poly vinyl alcohol (PVOH)
- silicone oil.

It was difficult to extrude some polymers in the Maxwell extruder, e.g., PMMA, Hypermer FP4, PPE (requires high temperatures), PEG, PEO (possibly due to low melt viscosity at 260°C). Some of the extrusion problems were possibly due to the low elasticity of the melt, since the pumping action in the Maxwell extruder (see Chapter 4.3) depends on that. Some polymers were seen to fume/vaporize easily in the extruder, e.g., Exxelor PO 1015 (flashpoint of 250°C) and Hypermer FP4 (flashpoint > 220 C). Even if pure polymers extruded easily, mixing was not achieved with the blends, e.g., nylon 6, PEO, PMMA and PC. Additionally, it was not possible to do melt annealing runs with some additives because of degradation problems, e.g., PEG 20 M, Separan AP 30.

To illustrate the lack of effect of blending, DSC annealing runs are shown for a 15% polymethyl methacrylate solution blend (Figures A.45 - A.49) and a 15% polyethylene oxide solution blend (Figures A.50 - A.52). T_c values for annealing the polymethyl methacrylate blend for a total time of 0, 30, 60, 80 and 100 mins are 238, 235, 232, 228 and 225°C, respectively. T_c values on annealing the polyethylene oxide blend for a total time of 0, 45 and 90 mins are 238, 236 and 235°C, respectively. The minimal effect on T_c is very apparent. In fact, there is a slight increase in T_c (238°C as compared with 236°C for pure nylon 6,6) for the as-prepared blend. Note that considerable amount of time was spent in the preparation and evaluation of all these blends. Usually each failure was followed by a time-consuming clean up of the extruder needing several days of work.

CHAPTER 6

SELECTION OF ADDITIVES & DESIGN OF DETAILED EXPERIMENTS

Several promising additives were identified from the screening experiments described earlier. These included both amorphous and semi-crystalline polymers, particularly nylons. Note that all the additives were commercially available ones. This implies that more effective additives could possibly be synthesized once the mechanism of additive action has been convincingly verified. An important concern was that the presence of the additive should not deteriorate the mechanical properties of nylon 6,6. In this regard it can be mentioned that recently published work by other workers [48] suggests that the addition of Trogamid-T to nylon 6,6 improves its fatigue properties. Also, as mentioned in the literature review, block copolymers normally show improved mechanical properties, as compared with random copolymers and the homopolymers themselves (see Section 3.2 and Table 3.1). Hence, this method, leading to the formation of block copolymers, as a material with reduced T_c, could prove successful.

The next stage in this work was to select additives to perform detailed experimentation. The selection was based on the following factors:

1) Extent of T_c suppression shown - this is the primary objective of this research.

2) Ease of melt processability - for commercial application, the additive should have the ability to be easily melt blended in an extruder.

3) Miscibility with nylon 6,6 - would influence initial level of mixing and hence the mechanical properties of the blend.

4) Thermal stability - since significant melt annealing is needed to produce required changes in thermal properties, the thermal stability of the additive becomes an important issue.

Based on the above considerations, two additives were selected: Trogamid-T (from the list of amorphous nylons) and nylon 6,12 (from the list of semi-crystalline nylons). Trogamid-T was selected since it appeared effective even at low concentrations. Solution blending appeared to give better results than melt blending for some blends. This suggests the need for a better understanding of the effect of mixing on the interaction between the polymers. Also, since annealing had a major influence on all the results, it is necessary to verify or disprove the occurrence of chemical reactions between the blend components.

During the initial experiments (described in the previous chapter), attention was not paid to the quality of the extrudate. The polymers were not dried and hence there could have been considerable changes in molecular weights and consequently melt viscosity, which, influences the quality of mixing. Also, the change in molecular weights can influence the nature and rate of interchange reactions. Appropriate attention was not given to the degradation of the polymer and this could affect the results obtained. Gelled material was noticed in the extrudate and this appeared because of degradation/oxidation. Degraded polymer could have altered thermal properties due to structural and molecular weight changes. Degraded material can also act as a nucleant and alter the rate of crystallization. Hence, it was important to eliminate the presence of such type of material.

In this stage of detailed experimentation, better quality samples were produced. All extrusion work was carried out on the twin screw extruder, which provides better dispersive and distributive mixing. The extruder was frequently cleaned (as described in Chapter 4.3) to ensure minimum degradation of the extrudate. Absence of degraded material was checked in the following ways:

(1) Visual inspection of the extrudate. Any discoloration (yellowing) of the extrudate suggests degradation.

(2) Comparison of the T_c of the extrudate to that of pure unextruded nylon 6,6. A significant increase in T_c is an indication of degradation (caused by the nucleating effect of the degraded material).

(3) Checking for the presence of gelled material by dissolving the extrudate in formic acid. The gelled material is insoluble in formic acid.

The polymer was dried to the required extent. The drying conditions, which led to a constant molecular weight and also an increase in molecular weight, were determined (described in the next section). Hence proper control, on molecular weight changes during extrusion, was exercised. In addition, all the prepared blends were stored in a desiccator capable of maintaining humidity at 20-30% at all times. This was to ensure minimum moisture pickup during sample storage.

6.1 Experimental Design

As mentioned earlier, further work was limited to blends with Trogamid-T and nylon 6,12. The variables examined were:

(1) *Additive type:* Amorphous nylon vs. crystalline nylon.

(2) *Additive concentration:* 10 vs. 5% wt/wt of the additives. Low concentrations were selected with commercial viability in mind. In addition, 25% wt/wt blends were also prepared,

for theoretical reasons.

(3) *Drying time:* Two drying times were to be determined:

- DT1, corresponding to a constant molecular weight.
- DT2, corresponding to an increase in molecular weight.

The following procedure was used to determine these drying conditions. Pure nylon 6,6 was dried for different times, at 100°C and under a vacuum of 2 mm Hg. The dried material was extruded on the twin screw extruder. IV measurements were conducted on the unextruded and the extruded samples of nylon 6,6 dried for different times. An increase in IV reflects an increase in molecular weight or postcondensation. By comparing differences in IV readings between the unextruded and extruded samples, at different drying times, the required drying time conditions were determined. Looking at the effect of interchange reactions on postcondensation was important, since in commercial processing, it is common to encounter melt conveying of nylon 6,6 during which postcondensation can occur.

(4) *Residence time:* Two residence times were used:

- 5 min (RT1) - normal extrusion.
- 30 min (RT2) - extrusion carried out by blocking the end of the die with a plug. Only a calculated amount of material was fed to the extruder (enough to fill the extruder under blocked conditions). Once the material had been fed to the extruder, the rpm was set at 30 and the extruder run for 30 min. At the end of this time period, the plug was removed and the extruded material collected in cold water. The initial material was discarded in the hope that only material actually sheared in the screws was collected. The initial material would have been inside the die and hence would not have received the additional shearing.

	Blends to be prepared			
	RT1[#] (5 min) DT1[*]	RT1 (5 min) DT1	RT2 (30 min) DT2	RT2 (30 min) DT2
Trogamid-T (10% wt/wt)				
Trogamid-T (5% wt/wt)				
Nylon 6,12 (10% wt/wt)				
Nylon 6,12 (5% wt/wt)				

[*] DT1 =drying time 1: mol. wt. increase: DT2=drying time 2: mol. wt. decrease

[#] RT=residence time in the extruder

The above 16 (2^4) blends needed to be prepared. In addition, 25% wt/wt blends of both the additives, were also to be prepared (8 blends).

6.2 Determination of Drying Conditions (Intrinsic Viscosity Measurements of Nylon 6,6)

Experiments were conducted, using the twin screw extruder, to determine the polymer drying and extrusion conditions necessary to achieve postcondensation and constant molecular weight. Initially, the IV readings showed significant variation. In particular, there were differences in readings between solutions made from the same polymer sample. Two possible sources of errors were identified:

(1) the concentration of 90% formic acid was changing on storage.

(2) the solutions used for the IV readings were sometimes stored for too long a time, leading to possible hydrolysis and change in molecular weights.

To correct these problems, a number of 100 ml bottles of 90% formic acid were purchased (better purity than before). These were of the same batch, ensuring the same concentration. A hydrometer (Cole-Parmer), capable of measuring up to 0.0005 g/ml was used to monitor density and hence indirectly the concentration. Also, the prepared solutions were analyzed within 2 hrs of preparation to prevent any possible changes in molecular weight due to hydrolysis.

Once the above conditions were adhered to, the precision of the readings improved to within that specified in the ISO 307. Successive reading differences became less than 0.4 s as well as the difference in IV readings of two solutions of the same sample were less than 2.0%. The actual measurements reported here were made after these satisfactory results were observed. The following drying experiments were conducted: IV measurements were made on unextruded polymer samples and on extruded samples, with different residence times. These included undried samples and ones dried for 2, 6 and 12 hrs. The results are shown in Table 6.1. Each reading is the average of five measurements. The drainage time (DT) for the solvent was 177.4 s. Residence times longer than 5 mins were achieved by blocking the end of the die of the extruder with a plug and letting the extruder run for the desired period of time. No distinction was made between the material that was in the barrel (sheared) and in the die (unsheared). Note that, in these experiments, only a measured amount of polymer was fed to the extruder. The hopper was not replenished once the polymer had entered the extruder.

The results appear to be internally consistent. The slight increase in DT on drying could be attributed to the presence of water in the pellets that was not taken into account in the sample weight. Hence, an undried sample of the same weight as a dried sample, will have

Table 6.1: Drainage Times (DT) of the Various Pure Nylon 6,6 Samples (s)

	Unextruded	Extruded RT=5 min	Extruded RT=15 min	Extruded RT=30 min	Extruded RT=60 min
Undried	279.9	279.5		287.6	
		275.6 (continuous extrusion)			
Dried 2 hrs	279.3	279.3			
6 hrs	280.4	280.2	283.0	288.6	288.2
12 hrs	280.6	280.6		287.6	

a slightly lower amount of nylon 6,6. This would result in a lower IV or drainage time. The results seem to indicate that under normal extrusion conditions, drying does not affect the polymer molecular weight. This is most likely due to the short residence time, which does not allow for postcondensation. Hydrolysis does occur during continuous extrusion with RT=5 min. When the residence time in the extruder, of the 6 and 12 hrs dried polymer, was changed to 30 min, the DT increased by roughly 7 s. This corresponds to an increase in molecular weight from approximately 15,858 to 17,393. The calculation is based on Eqs. 2 and 3 (Section 4.4), the viscosity number $[\eta]=KM^a$ with $k=11\times10^{-4}$ and $a=0.72$ and is given by $[\eta]=\{DT_{solution}/(DT_{solvent} - 1)\}/0.5$, where 0.5 is the concentration of the solution in g/dl.

The DT of the undried polymer did not decrease on increasing the RT. In fact, the DT's of the undried and samples dried for different times, are practically the same for RT=30 min. It was determined that devolatization was occurring in the extruder due to the short screw length. This was particularly true for the batch feeding conditions used in this work. Moisture was clearly seen to condense on the plexiglass hopper cover. This was not observed with the dried polymer, emphasizing the fact that the water volatized from the undried polymer is released into the hopper. The short screw possibly aided in this easy loss of vaporized water. Increasing the RT to 60 min, however, did not enhance this effect.

Later work confirmed that the feeding conditions did, in fact, lead to the devolatization mentioned above. Devolatization has been observed in extruders [49,50]. When continuous extrusion was carried out, i.e., with the hopper always kept full, no condensation was noticed. IV readings under these conditions showed a decrease, with DT for the undried sample going down to 275.6 s under extrusion conditions corresponding to 5 min RT (see Table 6.1). Hence, obtaining a decrease in IV under continuous extrusion conditions is possible. However, the longer residence times are not possible under these circumstances since these can only be obtained under batch feeding conditions.

Since it appears that the extent of drying is immaterial, provided the extruder is fed in a batch manner, any condition can be used (drying time of 6 hrs is selected). Since normal (batch) extrusion leads to no change in molecular weight, this will correspond to the control condition. A RT of 30 min can then be used as the condition corresponding to postcondensation.

6.3 Blend Formulations

The drying conditions were fixed, as described earlier. Since only one drying time was employed, the blends that need to be prepared were reduced. The variables that needed to examined now became:

(1) Type of additive - semicrystalline (nylon 6,12) vs. amorphous (Trogamid-T).

(2) Amount of additive - 5 vs. 10% wt/wt.

(3) Residence time - 5 vs. 30 min, with the higher RT also corresponding to postcondensation.

Hence the following blends were prepared:

- Nylon 6,6/Nylon 6,12:	5%, RT = 5 min
	5%, RT = 30 min
	10%, RT = 5 min
	10%, RT = 30 min
	25%, RT = 5 min
	25%, RT = 30 min
- Nylon 6,6/Trogamid-T:	5%, RT = 5 min
	5%, RT = 30 min
	10%, RT = 5 min
	10%, RT = 30 min
	25%, RT = 5 min
	25%, RT= 30 min

The above 12 blends were prepared in the twin screw extruder and stored in the desiccator.

CHAPTER 7

RESULTS & DISCUSSION

This chapter describes the results of the different types of experiments performed on the various blend samples prepared. These included intrinsic viscosity experiments, DSC non-isothermal and isothermal runs, extent of reaction, DMTA runs, polarized light microscopy and rheological experiments. Although blend samples of all concentrations were sought to be analyzed, in some cases only the 10% blends were studied to get an insight into the mechanism of additive action at low concentrations.

7.1 Intrinsic Viscosity Experiments of Blends (Effect of Drying Conditions)

Intrinsic viscosity (IV) measurements were made on Trogamid-T blends only, since nylon 6,12 is insoluble in formic acid; use of a different solvent and a different viscometer for analysis was not practical.

To examine the effect of reaction on molecular weight, IV measurements were made on 10% nylon 6,6/Trogamid-T samples with RT=5 and 30 mins. These were compared with the IV reading for a solution prepared by dissolving 90% by weight of nylon 6,6 pellets and 10% by weight of Trogamid-T pellets. The results (in terms of drainage time, DT) are shown in Table 7.1. There are no correlations available for relating DT for nylon 6,6/Trogamid-T blends to actual molecular weights. Hence, only qualitative conclusions, in terms of DT changes, can be drawn here. However, it is possible to compare the magnitude of the changes. It should be noted that an increase in DT signifies an increase in molecular weight and vice versa. The DT of the solvent (fresh batch) was 163.5 s. Note that a new viscometer (with a viscometer constant of 0.00811 as compared with 0.007500 centistokes/sec earlier) was used. The density of the 90% formic acid was monitored and held constant at 1.2025 g/ml for all the runs.

IV measurements were made with different samples from the same extrusion run. While the 5 min RT samples showed excellent repeatability, there were significant differences in the readings for the 30 min RT samples of the 10% blend. It should be noted that such variations were never encountered for unextruded polymers. Possible reasons for this inconsistency are discussed later. Although clear cut conclusions cannot be made from these data, a few trends are discernible and possible explanations are discussed below.

Table 7.1: Drainage Time (s) of the Various Nylon 6,6/Trogamid-T Blends

	Pellet mix	**RT=5 min**	**RT=30 min**
10% (wt/wt)	245.5	255.4	249.2
	245.8	255.5	248.8
			272.5
25% (wt/wt)	240.1	245.2	250.5
	240.8	246.3	249.7
			249.1

Comparing the readings for the 10 and 25% pellet mix, there is a decrease in DT when going to the higher additive concentration. This is only possible if the molecular weight of Trogamid-T is lower than nylon 6,6, since the only difference between the two pellet mixtures is the concentration of the individual polymers. Postcondensation and interchange reactions do not play any role here.

There is an increase in molecular weights for RT=5 min blends when compared with the pellet mix, clearly showing the effect of extrusion on the blend. This is in contrast to the behavior of pure nylon 6,6, where there was no change in molecular weight on batch extrusion with RT=5 min. For the case of pure nylon 6,6, there is no postcondensation during a regular (RT=5 min) extrusion. It should be remembered that transamidation reactions occur in a homopolymer but there would be no effect of these reactions on average molecular weight. This would suggest that initial interchange reactions in the blend, where block copolymers with long blocks are formed, lead to an increase in molecular weight, even though the additive is of a lower molecular weight. This would only be possible if diblock copolymers were being formed, i.e., the two homopolymers were attaching end to end. Hence it appears that the end group reactions are important in the initial stages. It will be shown later that nylon 6,6/Trogamid-T blends become miscible during regular (RT=5 min) extrusion as a result of interchange reactions and hence reaction can occur homogeneously throughout the entire blend volume. Hence there would possibly be a change from interfacial reaction to bulk reaction during the course of extrusion.

The increase in molecular weight is more for the 10% blend (~10 s) when compared with the 25% blend (~5 s). Two factors become important here. Firstly, the molecular weight of the additive is lower and hence there should be an effect on increasing the concentration of the additive. Secondly, there would be more reaction at the higher additive concentration, especially when the homopolymers become miscible. It would then seem to appear that reactions in the later stages cause a decrease in molecular weight. It should be noted that as the molecular weight increases, the end group concentration will decrease and hence the extent of end group reactions will alos decrease. It is possible that under these conditions the amidolysis (amide to amide reaction) can become more significant and this would cause a decrease in average molecular weight.

There is a slight decrease (ignoring the high reading) on increasing the residence time for the 10% blend and a slight increase for the case of the 25% blend. This is in contrast to the significant increase in molecular weight for pure nylon 6,6 RT=30 min samples. Since devolatization/postcondensation should occur under these conditions, it appears that prolonged reactions actually result in a decrease in molecular weight. The higher residence time leads to postcondensation in pure nylon 6,6 (as shown earlier) and an increase in molecular weight. Hence it would appear that the net effect of interchange reactions is to counteract postcondensation and these could be competing processes. This would then support the speculation made previously, that molecular weights were decreasing in the latter stages of the reaction. Since higher residence can only be achieved under batch conditions, with the die blocked, the effect of devolatization may become critical since it can affect the interchange reactions via the end group concentration. However, the above discussion cannot explain the increase in molecular weight for the 25% blend on increasing the residence time. If we examine the net change in DT of the two blends, there is a increase of ~ 4.5 s for the 10% RT=30 min blend and an increase of ~10 s for the 25% RT=30 min blend. These changes are of the same magnitude as pure nylon 6,6 RT=30 min sample (~8 s).

Another factor that needs to be considered is the molecular weight distribution

(MWD). The interchange reactions can have a pronounced effect on MWD, especially if the two polymers have initial differences in molecular weights. In addition, the two polymers themselves could have a large MWD. Under these conditions, the block copolymers formed could have a dramatically different MWD and hence average molecular weight. Since IV can only measure an average molecular weight (M_v), the method is not capable of distinguishing between two systems that have a widely different MWD but the same M_v. In addition possible degradation could be causing a decrease in the molecular weight.

The other noticeable point was that both the pellet solution and the RT=5 min solution had a whitish appearance. Dissolution of pure Trogamid-T results in a whitish solution. However, the RT=30 min sample resulted in a clear solution, identical to a pure nylon 6,6 solution, for both the 10% and the 25% blend. This strongly suggests that Trogamid-T could be getting incorporated into block copolymer with nylon 6,6, and these are readily soluble in formic acid, as compared with pure Trogamid-T.

It can be seen from Table 7.1 that for the 10% blend, there is a dramatic difference in the DT of the RT=30 min samples. It was observed that some portions of the extruded filaments had dense material with a different appearance. Even during the actual process of extrusion this kind of material was noticed, since it was difficult to extrude due to the high melt viscosity. It appears that this material has a very high molecular weight and is possibly formed due to the dead spaces in the mixing gaps of the screws. Hence this material will have a very high residence time and consequently a very high molecular weight. Such high molecular weight material has been observed by other workers [51]. It was found that polymers prepared by extended melt polymerization in inert atmospheres showed high vaules of [η]. A plausible explanation was the increase of the polycondensation to progressively higher levels accompanied by branching reactions. IV reading on a sample from this kind of material showed similar high drainage time (267.2 s) while samples from the regular portion gave consistent readings. On the other hand, there could be differences in the molecular weights of the sheared and the unsheared material, suggesting that reaction leads to an increase in molecular weight. However, with the 25% RT=30 min blend there was practically no variation in the readings taken for 3 samples.

Local variations in blend composition and residence time have been reported [51]. These are of the order of magnitude of milligrams (size of DSC samples or IV samples). Significant molecular weight fluctuations can occur as a result of blending of polymer pellets and due to poor mixing [23]. Although interchange reactions and mixing processes can reduce the size and degree of these rheologically different volume elements, these heterogeneities can still persist at a macroscale. High molecular weight pellet contaminant does have a high persistence as a rheological volume element. This was studied by Kotliar [23] by conduction of force trace experiments in an Instron rheometer. Hence, it is possible that these rheologically different volume elements are responsible for differences in IV readings. The fact that backmixing exists in the twin screw extruder further complicates the issue.

In conclusion it can be said that although the IV experiments were to some extent inconclusive, they provided a very useful insight into what possibly happens during the time period interchange reactions are actively occuring. In addition, there was a very useful intuitive insight into the mechanism of reaction and the effect of these reactions on the molecular weight. From a commercial viewpoint, the significance of these interchange reactions on postcondensation and molecular weight is important, since polymer processing times are in the range discussed above. The relationship between the interchange reactions and the competing postcondensation necessarily affects molecular weight and can be critical in the processing of these types of reactive blends.

7.2 DSC Runs

Most of the blend samples were analyzed using various DSC techniques. These included non-isothermal runs (to compare T_c's); isothermal runs (to compare actual crystallization times); Hoffman-Week's plots (to determine equilibrium melting point T_m^o) and hence the extent of reaction. These results are discussed in this section.

7.2.1 Non-Isothermal Runs

Non-isothermal runs were carried out on the blends. The following procedure was used to analyze all the samples:

-Equilibrate at 5°C

-Ramp at 10°C/min to 300°C

-Isothermal for 5 min

-Ramp at 5°C/min to 50°C

The melting point was determined as the peak of the endotherm in the heating run and the crystallization temperature was determined as the peak of the exotherm in the cooling run. All samples were annealed for 0, 1, 2, 3 and 4 hrs and the T_m and T_c values were recorded. This was to see the effect of annealing on the thermal behavior of the blends.

The as-prepared 25% nylon 6,6/Trogamid-T blend (RT=5 min) has a T_c of 221.7 °C (Figure 7.1), which decreases to 200.6°C after annealing for 4 hrs (Figure 7.2). Since the T_c of pure nylon 6,6 is 236°C, there is a decrease of almost 35°C after 4 hrs of annealing in the melt. The T_m of the as-prepared sample is 260.2°C (Figure 7.1), close to that of pure nylon 6,6 (263°C), which reduces to 239.4°C after 4 hrs of annealing (Figure 7.2). The effect on the crystallization behavior is more significant as compared with the melting behavior. This can be explained in terms of the structure of the block copolymers that are formed. The incorporation of non-crystallizable segments in the crystallizable segments of nylon 6,6 impedes the process of crystallization. This is reflected by a decrease in T_c and a broadening of the crystallization exotherm. Both are indicative of a decrease in the rate of crystallization. The effect of reduced rate of crystallization is also the formation of imperfect crystals which melt at a lower temperature.

Results for all the nylon 6,6/Trogamid-T blends are shown in Table 7.2 (in terms of T_c and T_m) and are consistent with the results obtained earlier. The actual thermograms are reported in Appendix B (Figures B.1 to B.30). Significant effects (of a correspondingly lesser extent) are seen at lower additive concentrations of 10 and 5% wt/wt. The data are consistent, and T_c values of the unannealed samples decrease as the concentration is increased. The T_c values are 235.1, 230.4 and 221.7°C for the 25, 10 and 5% blends, respectively. Recent work [52-55] has shown similar changes in the thermal behavior for nylon 46 (crystalline) and nylon 6I (amorphous) blends. The T_c and T_m values decreased as the extrusion time was increased. The effect of concentration [52] was similar to what was observed in this work. It was also observed that increasing the extrusion temperature produced faster changes in thermal

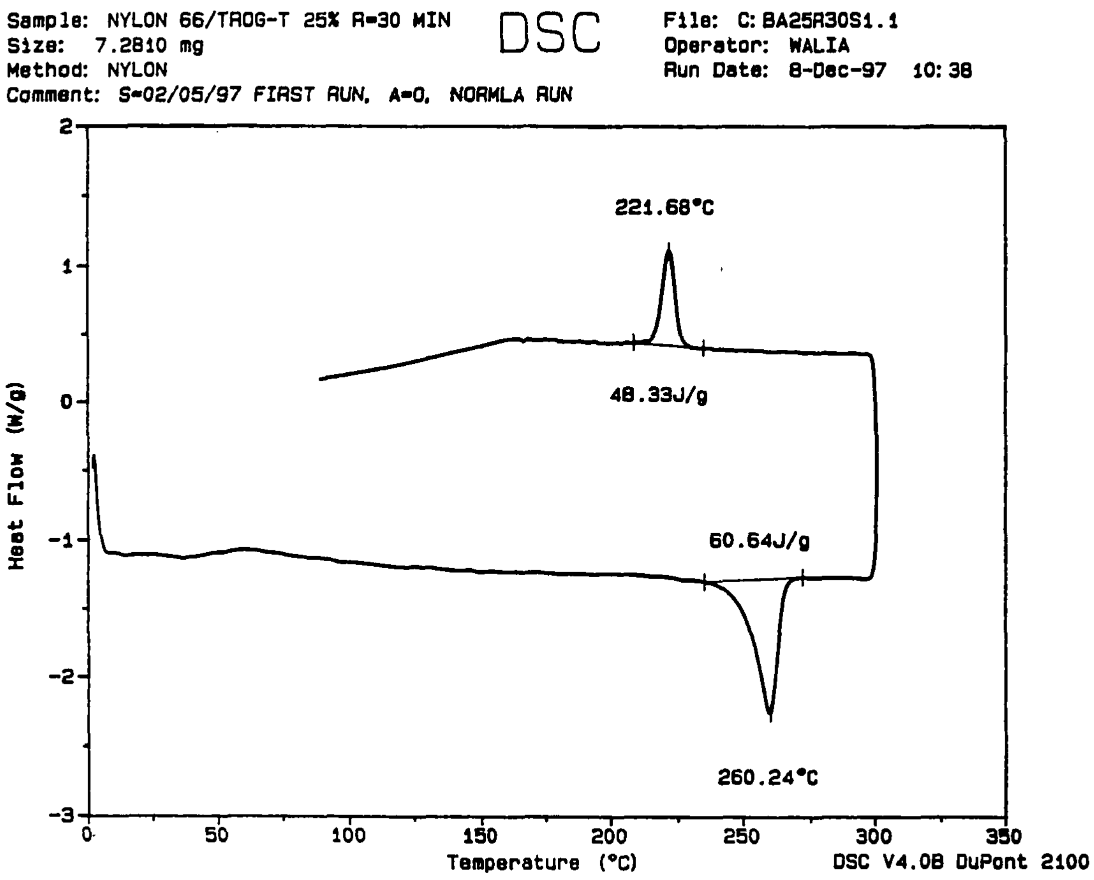


Figure 7.1: DSC run for the as-prepared 25% nylon 6,6/Trogamid-T blend (RT=5 min)

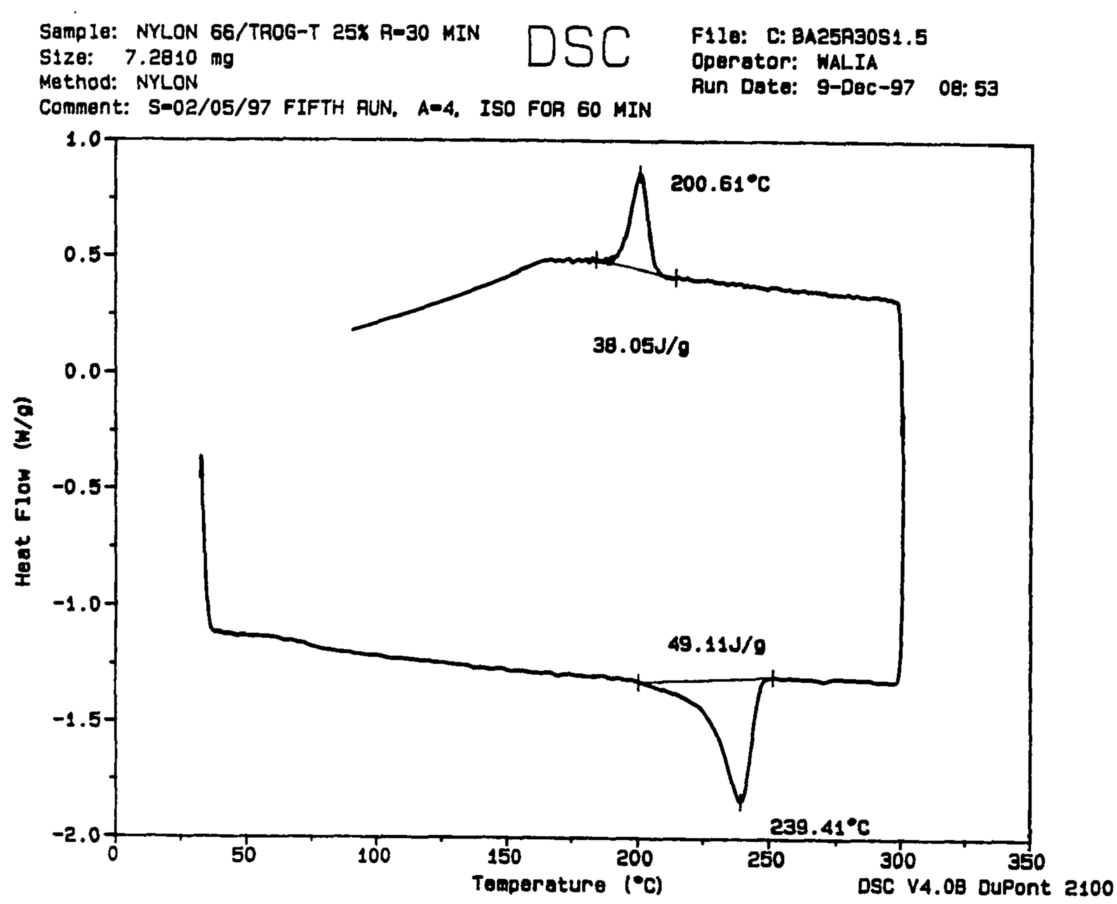


Figure 7.2: DSC run for 25% nylon 6,6/Trogamid-T blend (RT=5 min) annealed for 4 hrs

behavior, similar to the effect of extrusion time.

Table 7.2a: Effect of Annealing Time (hrs) on T_c of Nylon 6,6/Trogamid-T Blends					
	0	1	2	3	4
25% RT=5 min	221.7	217.5	213.1	206.4	200.6
25% RT=30 min	218.5	214.9	206.1	198.6	191.7
10% RT=5 min	230.4	225.1	218.0	209.7	203.5
10% RT=30 min	227.3	225.1	218.4	209.4	199.8
5% RT=5 min	235.1	234.1	232.4	229.7	224.8
5% RT=30 min	233.5	229.9	226.2	221.3	216.4

Table 7.2b: Effect of Annealing Time (hrs) on T_m of Nylon 6,6/Trogamid-T Blends					
	0	1	2	3	4
25% RT=5 min	262.1	256.1	253.2	245.5	238.4
25% RT=30 min	260.2	255.4	251.6	244.0	239.4
10% RT=5 min	261.5	259.3	255.3	246.5	239.5
10% RT=30 min	261.0	258.1	255.9	247.2	240.9
5% RT=5 min	262.3	260.8	259.8	258.1	255.8
5% RT=30 min	261.5	260.0	256.8	249.3	247.0

Results for the nylon 6,6/nylon 6,12 blends, in terms of T_m and T_c, are summarized in Table 7.3. The corresponding thermograms are reported in Appendix B (Figures B.31 to B.60 respectively). The behavior of the blends was exactly the same as with the earlier prepared blend samples. Two melting and crystallization peaks were detected for the unannealed blends, at the 25 and 10% concentration levels. These merged into single melting and crystallization peaks on annealing the samples for 1 hr. However, surprisingly, for the case of 5% blend, the nylon 6,12 melting endotherm could not be detected. Either there was a problem of attaining uniform composition in the twin screw extruder or the interchange reactions were fast enough to incorporate this low level of nylon 6,12 into copolymers. All RT=30 min blend samples showed single melting and crystallization transitions, indicating that practically only copolymers (block/random) are present at this stage of the reaction. Again this suggests a fast rate of interchange between these semi-crystalline polymers.

Table 7.3a: Effect of Annealing Time (hrs) on T_c of Nylon 6,6/Nylon 6,12 Blends

	0	1	2	3	4
25% RT=5 min	233.2	225.3	222.4	213.7	204.8
25% RT=30 min	221.9	212.3	209.0	200.8	194.3
10% RT=5 min	233.2	228.0	222.2	217.9	212.4
10% RT=30 min	231.8	230.9	226.5	219.4	211.6
5% RT=5 min	234.8	233.8	231.7	228.3	223.7
5% RT=30 min	233.3	229.5	224.6	218.0	211.0

Table 7.3b: Effect of Annealing Time (hrs) on T_m of Nylon 6,6/Nylon 6,12 Blends

	0	1	2	3	4
25% RT=5 min	262.4	260.1	248.9	245.0	241.0
25% RT=30 min	257.6	252.3	241.7	237.8	230.6
10% RT=5 min	263.5	260.9	255.4	247.8	244.9
10% RT=30 min	259.5	258.2	250.5	248.9	244.2
5% RT=5 min	260.7	259.9	258.2	249.2	248.0
5% RT=30 min	262.2	258.2	250.1	247.6	243.4

The trend appears to be the same as reported for the Trogamid-T blend. The T_c

decreases as the melt annealing time increases. However, there is practically no difference in T_c of the as-prepared blends of different concentrations. The miscibility of the nylon 6,12 with nylon 6,6 has to be questioned here. If the two nylons are not miscible to start with, initial reaction will be small due to the low interfacial area and only small changes in T_c will result. Hence, the effect of concentration will not be prominent in the initial stages.

The results are consistent for all RT=5 min blend samples. However, for the 25% blend with RT=30 min, there is a significantly higher suppression of T_c for the as-prepared blend sample. The T_c value is 221.9 °C, almost 13°C lower than the RT=5 min blend. Such significant differences are not present for the 10 and 5% RT=5 and 30 min as-prepared samples. The T_c value for the 25% RT=30 min sample is even lower than the T_c value for RT=5 min sample that has been annealed for 1 hr (225.3°C). This would suggest that additional mixing is promoting faster reactions. The 5% RT=30 min unannealed sample also shows a T_c value (233.3°C) lower than that of the 5% RT=5 min sample annealed for 1 hr. However, there is no significant difference in the T_c values of the 10% RT=30 min blend with RT=5 and 30 mins. The T_c value for the 10% RT=30 min sample is intermediate between the T_c values of the 10% RT=5 min samples annealed for 0 and 1 hrs. Effect of residence time will be discussed later, in Section 7.2.3

On annealing, the 10% RT=30 min sample shows the same changes as the 10% RT=5 min sample. However, the 5% RT=30 min sample shows more pronounced changes compared with the 5% RT=5 min sample. On annealing for 4 hrs, there is a difference of almost 12°C between the T_c values of the RT=5 min and 30 min samples. Hence there is a certain degree of inconsistency in these results.

Comparing the data for the two types of blends, it can clearly be seen that the reduction in T_c is greater for the Trogamid-T blend. This is true at any blend concentration. The reduction in T_c is also greater for the as-prepared blend indicating faster interchange during melt mixing or a bigger effect of these reactions on the crystallization kinetics. However, the change in T_c on annealing for 4 hrs is relatively the same . This possibly suggests that the rate of interchange reactions is relatively the same. It should be noted that since interchange reactions are not being measured directly, it is possible that the reaction could be faster in one case, although the effect of these reactions on T_c or T_m maybe not that significant.

The reduction in the rate of crystallization appears to be caused due to the incorporation of non-crystallizable segments (for the case of amorphous nylon) or structurally dissimilar crystallizable segments (for the case of semi-crystalline nylon). Although the higher suppression for the case of Trogamid-T blends can be explained by this effect, the miscibility of the blends needs to be taken into account. As will be shown, Trogamid-T is miscible or nearly miscible with nylon 6,6 and hence its blends will have high interfacial area leading to faster reaction. The miscibility of nylon 6,12 with nylon 6,6 was difficult to address. In addition, there could be inherent differences in the rate of interchange reactions of Trogamid-T and nylon 6,12 with nylon 6,6. All these effects would be reflected in the T_c reduction as a function of annealing time.

7.2.2 Effect of Blending Method

Table 7.4 compares the change in T_c of the melt and solution prepared blends. For the case of the 10% blend, it can clearly be seen that the solution blend shows a much larger decrease in T_c when compared with the melt blend. Comparing the 25% melt blend to the 20% solution blend, it can be seen that even at a lower concentration, the solution blend gives a lower T_c value. The T_c values of the melt and solution unannealed blends are similar, but lower than that of pure nylon 6,6. This would suggest that the same degree of reaction takes place in both the blend preparation methods. Although no time is spent in the melt during solution blending, there is a significant amount of time that is spent at temperatures of 70-80°C during the solution preparation and evaporation. This is likely to influence the results. It needs to be mentioned that Trogamid-T does not easily dissolve in formic acid and has to be heated to 80-90°C to complete the dissolution. Therefore, the possibility of interchange reactions in solution does exist.

It can clearly be seen that on melt annealing, the solution blend shows significantly larger changes in T_c. This would suggest that the initial level of mixing plays an important role in determining the extent of reaction, since the solution blend is expected to be intimately mixed. However, the role of elevated solvent temperatures cannot be totally ignored. It will be shown later that nylon 6,6/Trogamid-T blends prepared on the twin screw extruder are miscible and should mix on a molecular level during blending. It should also be noted that determining T_c inherently involves holding the sample at 300°C for 5 mins and interchange reactions would invariably occur during this time. Hence the fact that the unannealed solution blend shows a T_c value similar to the melt blend suggests that reactions are occurring faster in the solution blends. This again supports the idea that the solution blend is better mixed and hence has more interfacial area available for reaction. The above observation is contrary to that of Eersels et al. [52, 53] who observed larger reductions with the melt blends of nylon 46 and nylon 6I.

Table 7.4: Comparison of T_c values (°C) of solution/melt* blends of nylon 6,6/Trogamid-T annealed for different times (hrs)

	0	0.5	1	1.5	2
25% melt blend	221.7		217.5		213.1
20% solution blend	225	220	205	175	
10% melt blend	230.4		225.1		218.0
10% solution blend	227	211	203	183	

*Prepared on the Maxwell extruder

7.2.3 Effect of Residence Time

It is important to look at the effect of residence time on the interchange reactions. Commercially, different residence times can be encountered not only during polymer processing but also during the conveying of the molten polymer. The effect of the higher residence time can be seen clearly, with T_c decreasing at the higher residence time. However, looking at Table 7.2a, it can be seen that there is no significant change in thermal behavior of the Trogamid-T blends by increasing the residence time in the extruder as compared with simple annealing in the DSC. All RT=30 min samples have a T_c value that is intermediate between the T_c values of the unannealed and 1 hr annealed RT=5 min samples. For example, for the case of Trogamid-T blends, T_c values for 25% RT=5 min sample for A=0 and A=1 hrs are 221.7 and 217.5°C respectively, whereas the T_c value for 25% RT=30 min sample is 218.5°C. This suggests that there is no significant increase in reaction as a result of shearing in the extruder. Although the possibility exists that T_c probably may not be a sensitive enough parameter to measure the extent of reaction. It will be shown later (Chapter 7.3) that nylon 6,6 and Trogamid-T blends become miscible in the initial stages of the reaction. Under these conditions the two polymers will be mixed on a molecular level and completely dispersed blends will be formed at the beginning. Hence shearing the sample will not promote any additional reactions. Eersels et al. [53] observed no differences on increasing the screw rotational speeds, during the melt blending of nylon 46 and nylon 6I. The blend was reported to be miscible and it was concluded that because of miscibility, interchange reactions are not enhanced on intensive mixing. On the other hand, if the blend was immiscible, then additional shearing will create more interfacial area and promote additional reactions.

There were effects of residence time for the nylon 6,12 blends, as discussed earlier (see Tables 7.3a and 7.3b). The 25 and 5% RT=30 min samples showed higher suppressions in T_c than what is observed on static DSC melt annealing. This would suggest initial immiscible blends where interfacial area (and hence interchange reaction) is increased by additional shearing. The melt miscibility of nylon 6,12 with nylon 6,6 was not studied. Data available from literature suggest that the two polymers are immiscible [56], but the effect of interchange reactions on miscibilty is unknown. However, the DSC data support the fact that miscibility would result in this blend system. Earlier (Chapter 5.4.1, and Figures A.37 - A.39 in Appendix A) it was reported that a 25% nylon 6,6/nylon 6,12 blend showed a single melting and crystallization peak on repeated DSC runs. The complete disappearance of the identity of nylon 6,12 implies that all of nylon 6,12 got incorporated into block copolymers. These copolymers act as emulsifiers and reduce interface tension. Hence, the phase boundary between the two nylons is eliminated. The copolymers are expected to be mutually miscible and hence a miscible system should result. Since cocrystallization occurs very rapidly (~10 mins), miscibility should result during the same time span. During the high residence time runs, due to more intensive mixing as compared with simple melt annealing, miscibility should result faster. Even before complete miscibility is achieved, better mixing would result during the RT=30 min extrusion because of continous shearing. Hence, it can be expected that interchange reactions would occur faster for the RT=30 min sample. There would then be a corresponding more pronounced effect on thermal properties on melt annealing. The data for the nylon 6,12 blends seem to support the above view (10% RT=30 min results are an exception).

7.2.4 Effect of Catalyst

The above experiments showed that the transamidation reactions are slow, especially at low concentrations of the additive. Since annealing in the melt for long times is unfeasible, due to potential problems associated with degradation, it was decided to investigate the effect of a catalyst. Triphenyl phosphite (TPP) was used in an attempt to speed up the transamidation reactions. This catalyst was chosen based on a review of the literature [30, 31], as reported in Chapter 3.2.

Since TPP is a liquid at room temperature, preblending this material with the blend posed a problem. An approximate amount of TPP (1% wt/wt) was added to the polymer pellets so as to completely wet them. On extrusion, though, the wet pellets began to fume and it was difficult to determine how much of the added TPP actually remained in the final blend. The following three samples were prepared:

(i) Nylon 6,6 + TPP

(ii) Nylon 6,6/ Zytel 330 (10% wt/wt) + TPP

(iii) Nylon 6,6/Zytel 330 (10% wt/wt) - No catalyst.

The blend samples were analyzed using non-isothermal DSC runs. Thermograms were obtained of the as-prepared samples and also of samples that had been annealed in the melt at 300°C for 2 hours. While the presence of the TPP in nylon 6,6 did result in minor changes in the peak temperatures with annealing (Figures 7.3 & 7.4), the catalyst affected the blend samples in a much more significant way. The T_c values for the unannealed, extruded samples of pure nylon 6,6 are 236°C without the catalyst and 232°C with the catalyst. Hence, extrusion with TPP leads to a slight depression in T_c, which can be attributed to the increase in molecular weight due to increase in chain length. On annealing the samples for 2 hrs, the T_c was 232°C without the catalyst and 227°C with the catalyst. The small decrease in the values is probably a result of degradation due to the long melt annealing. However, the difference in the T_c values does not increase (5°C compared with 4°C earlier). Figure 7.5 compares the thermograms of the as-prepared 10% nylon 6,6/Zytel 330 blends, with and without the catalyst. It can clearly be seen that the use of the catalyst has resulted in an 8°C lowering of the T_c relative to the sample without the catalyst. On annealing for 2 hrs, the difference in T_c increases to 25°C, as seen in Figure 7.6, which compares the thermograms of the 10% nylon 6,6/Zytel 330 samples annealed for 2 hrs, with and without the catalyst. The difference in T_c on annealing increases dramatically for the blend whereas there is no change for the case of pure nylon 6,6. This clearly demonstrates the effectiveness of the catalyst.

As discussed in Chapter 3.2, TPP causes an increase in chain length of nylons through

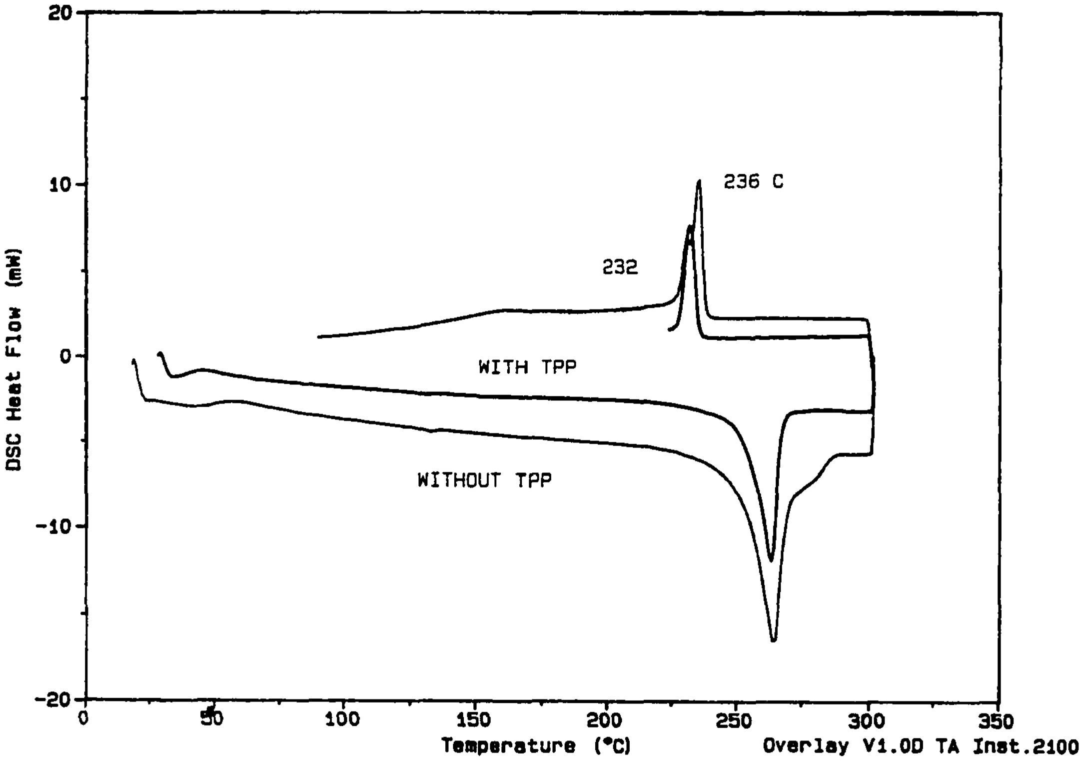


Figure 7.3: DSC run for nylon 6,6 - with and without TPP (unannealed)

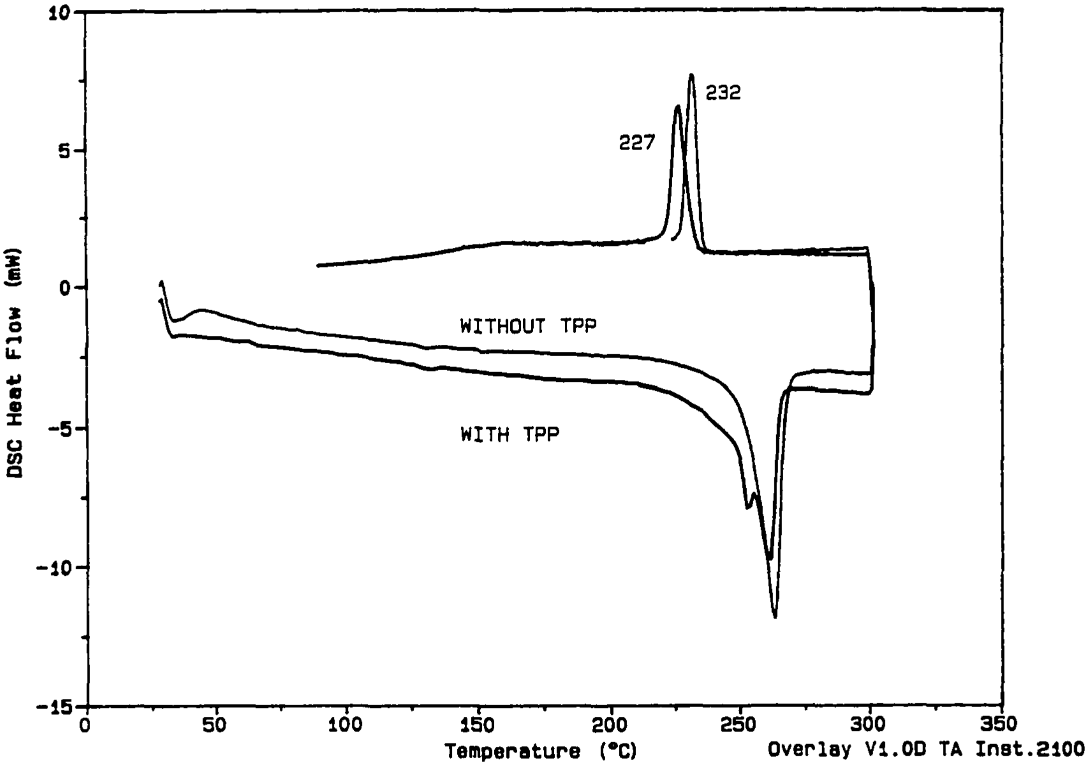


Figure 7.4: DSC run for nylon 6,6 - with and without TPP (annealed for 2 hrs)

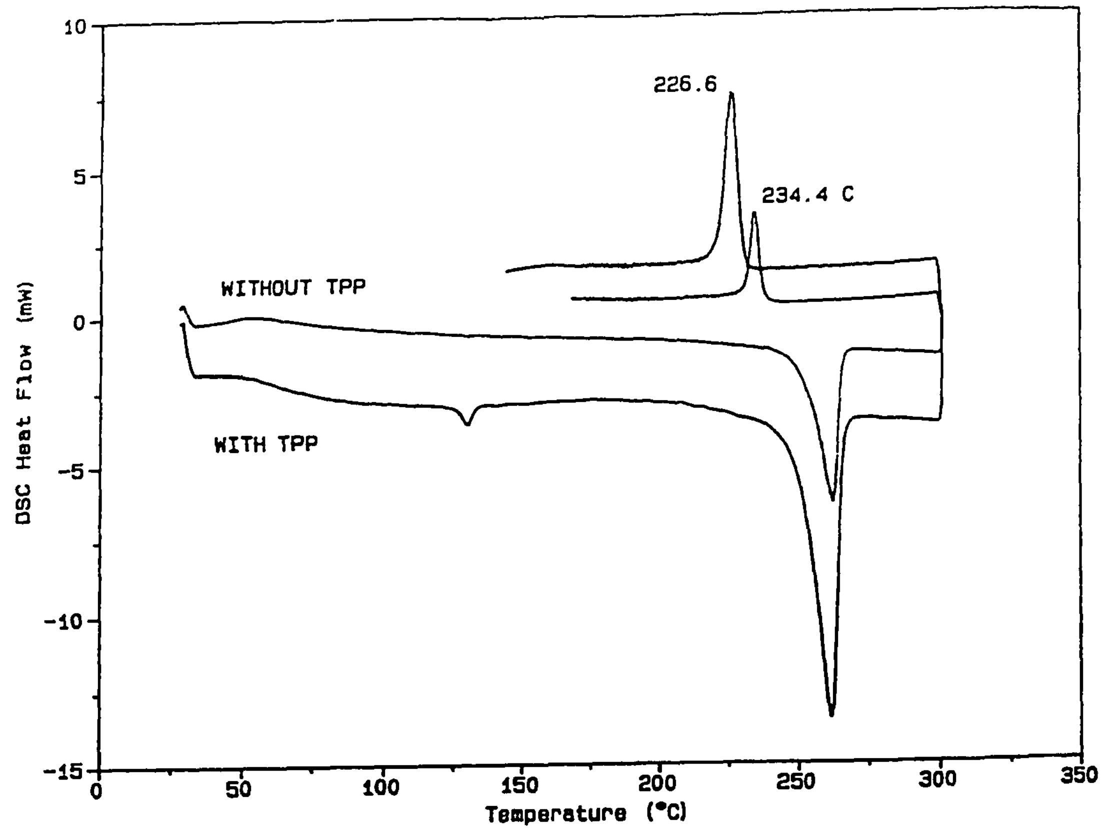


Figure 7.5: DSC run for 10% nylon 6,6/Zytel 330 - with and without TPP (unannealed)

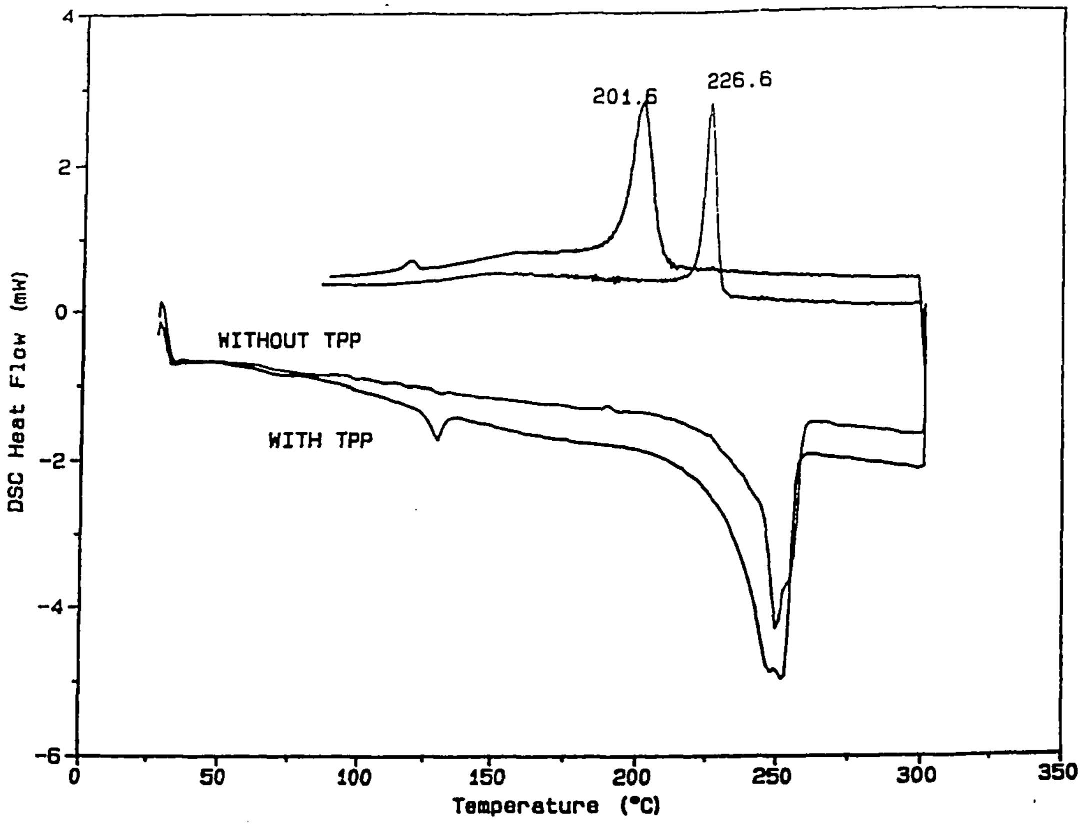


Figure 7.6: DSC run for 10% nylon 6,6/Zytel 330 - with and without TPP (annealed for 2 hrs)

the formation of amide bonds during melt blending. In the case of a single polymer, this will result in the increase of molecular weight and a corresponding decrease in the rate of crystallization. However, for the case of well mixed polymer blends, this will result in possible amide linkages between the end groups of the blend components, leading to the formation of block copolymers and a concurrent increase in molecular weight. The fact that the effect of interchange reactions is much greater than that of molecular weight increase, was clearly established. Although the mechanism by which the catalyst promotes interchange reactions is not known, TPP does show potential for significantly increasing the rate of interchange reactions.

7.2.5 Isothermal Runs

Isothermal runs were made by heating the sample to 300°C and holding it there for 5 min. Then the sample was rapidly quenched to the desired temperature and held isothermal until the crystallization process was completed. Specifically, the following program was used to analyze the samples:

- Equilibrate at 150°C
- Ramp at 10°C/min to 300°C
- Isothermal for 5 min
- Ramp at 200°C/min to the required isothermal temperature, T_c
- Isothermal for 60 min

The run could be terminated when the crystallization process was over. The heating run after the isothermal run was used to determine the T_m resulting from the previous isothermal run.

There is only a narrow window of temperatures at which isothermal crystallization runs can be conducted. At low temperatures, crystallization becomes too fast and at high temperatures, too slow to be accurately measured by the DSC.

Table 7.5: Total crystallization time (min) at different isothermal temperatures for the 10% nylon 6,6/Trogamid-T (RT=5 min) blend (annealed for different times)

Crystallization Temperature T_c (°C)	Nylon 6,6	Blend, A=0 hr	Blend, A=1 hr	Blend, A=2 hr	Blend, A=3 hr	Blend, A=4 hr
195						3.20
200						5.41
205					4.01	12.41
210					6.90	
215				1.39	16.74	
220			2.02	3.71		
225	0.69	1.45	3.02	6.03		
230	0.86	2.05	11.71			
235	2.10	2.93				
240						
244	8.31					

Table 7.5 shows the total time taken for crystallization at the different isothermal temperatures for the case of a 10% nylon 6,6/Trogamid-T blend (RT=5 min) annealed for different times (actual isothermal thermograms for samples annealed for different times are presented in Appendix C, Figures C.1 to C.19). Total crystallization time is measured as the time difference between the beginning and the end of the exotherm (see Section 4.5 and Figures 4.7 and 4.8). Figure 7.7 shows the plot of total crystallization time versus the

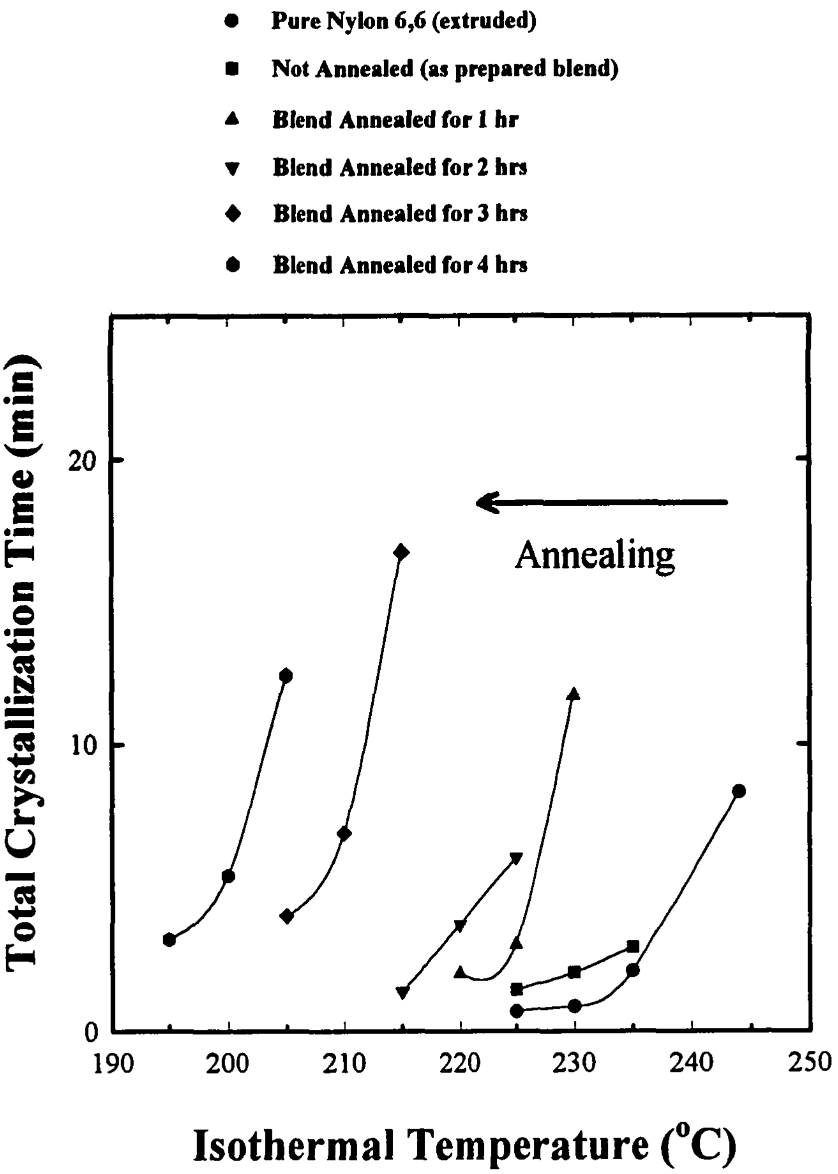


Figure 7.7: Isothermal Crystallization Plots for a 10% Nylon 6,6/Trogamid-T (RT= 5 min) Blend Annealed for Different Times, as Compared with Pure Nylon 6,6

isothermal crystallization temperature. It can clearly be seen that as the sample is annealed, the crystallization time increases dramatically, especially in the higher temperature range. For example, at 225°C, the total crystallization time increases from 0.69 min for pure nylon 6,6; to 6 min for the blend annealed for 2 hrs; and too slow to be detected for the blend sample annealed for 4 hrs. This agrees with the non-isothermal data reported earlier, showing significant reductions in T_c.

Table 7.6: Total crystallization time (min) at different isothermal temperatures for the 10% nylon 6,6/nylon 6,12 (RT=5 min) blend (annealed for different times)

Crystallization Temperature T_c (°C)	Nylon 6,6	Blend, A=0 hr	Blend, A=1 hr	Blend, A=2 hr	Blend, A=3 hr	Blend, A=4 hr
210					2.72	
215					3.57	
220		1.27			6.46	7.39
225	0.69	1.95	2.00	3.05	24.65	46.41
230	0.86	3.14	3.37	3.43		
235	2.10	3.74	8.70	15.80		
238		11.36	17.09			
240						
244	8.31					

Figure 7.8 shows similar isothermal crystallization data for the 10% RT=5 min nylon 6,6/nylon 6,12 blend. The data are tabulated in Table 7.6 (actual thermograms are shown in Appendix C, Figures C.20 to C.37). The trend is the same but the reduction in crystallization rates is smaller as compared with the 10% Trogamid-T blend. This can be seen more clearly in Figure 7.9 which compares the isothermal crystallization times of the two blends. This is

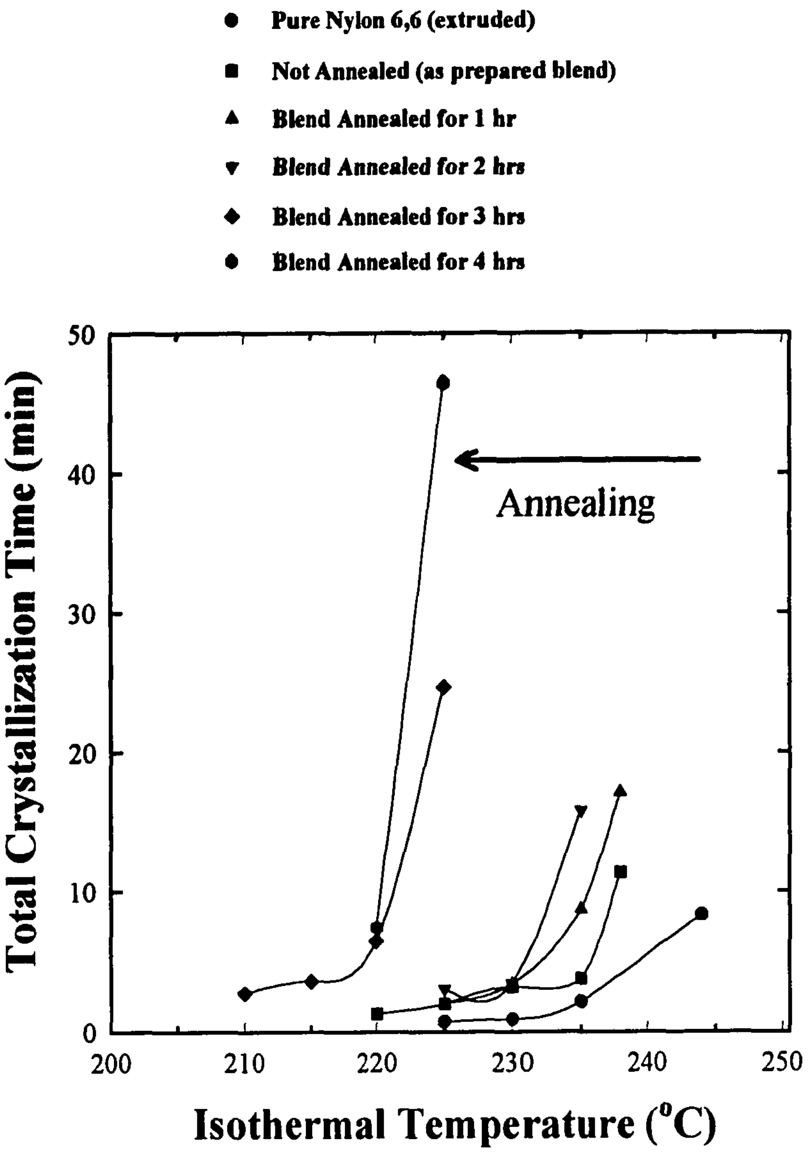


Figure 7.8: Isothermal Crystallization Plots for a 10% Nylon 6,6/Nylon 6,12 (RT= 5 min) Blend Annealed for Different Times, as Compared with Pure Nylon 6,6

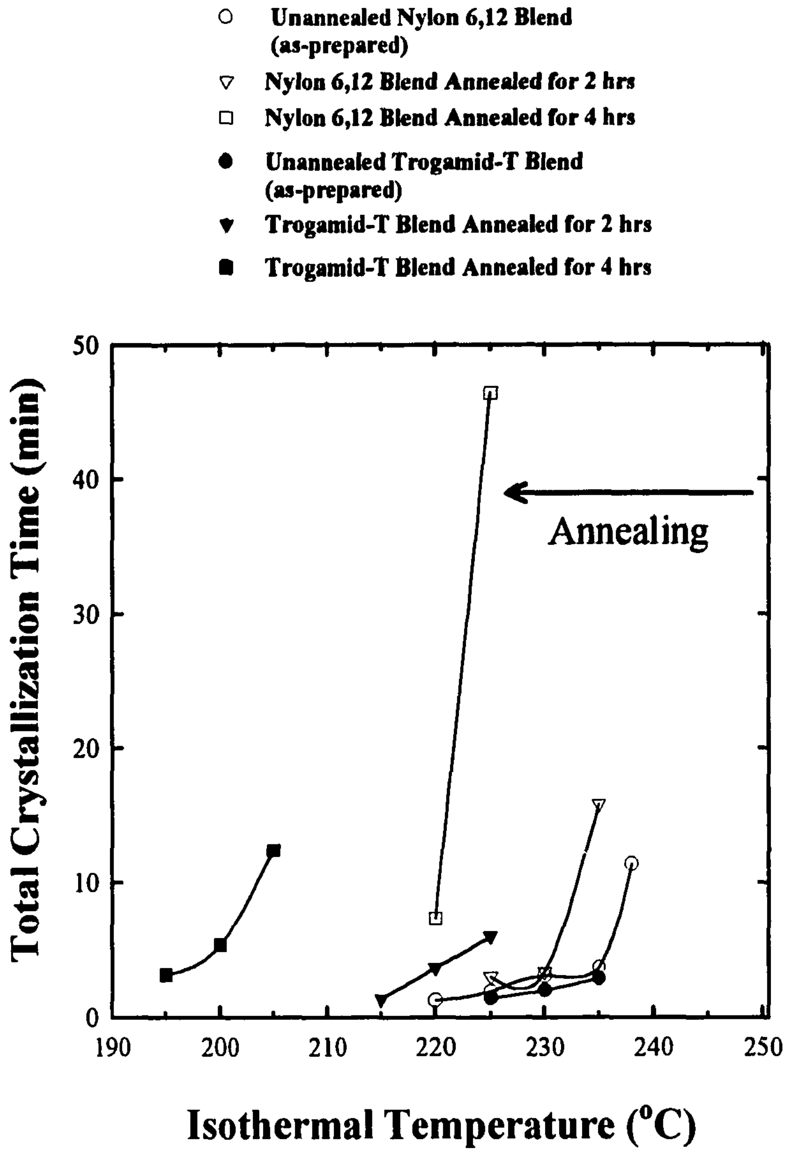


Figure 7.9: Comparison of Isothermal Crystallization Plots of the 10% (RT=5 min) Blends of Trogamid-T and Nylon 6,12

consistent with the non-isothermal data where the reductions in T_c were larger for the Trogamid-T blend. This would imply either faster interchange reactions for the Trogamid-T blend or a larger effect on the crystallization process due to the formation of block copolymers, suggesting that the block copolymers of Trogamid-T have a lower ability to crystallize. Additionally, initial miscibility will also play an important role here.

7.2.6 Hoffman-Weeks Plots & Extent of Reaction

The equilibrium melting point, T_m^o, was determined by means of a Hoffman-Weeks plot. The sample was crystallized at different isothermal temperatures (T_c). After the isothermal crystallization run, the melting point was determined by heating the sample at 10°C/min and noting the peak of the melting endotherm as T_m.

To determine T_m^o, T_m was plotted against T_c and the data extrapolated to the line $T_m=T_c$. The point of intersection is the T_m^o. This was carried out for the as-prepared sample and for samples annealed for different times. This is shown in Figure 7.10, for the case of the 10% nylon 6,6/Trogamid-T (RT=5 min) blend and in Figure 7.11, for the case of the 10% nylon 6,6/nylon 6,12 (RT=5 min) blend. The data are fairly linear for all the samples and a continuous decrease in T_m^o can be clearly seen. The T_m^o for the unannealed and samples annealed for 1, 2, 3 and 4 hrs is 262.0, 253.0, 247.0, 238.0, 233.0 °C respectively, for the 10% Trogamid-T blend. Corresponding values for the nylon 6,12 blends are 261.5, 258.1, 255.2, 250.2 and 244.1 °C respectively.

The T_m^o was plotted as a function of annealing time for the case of 10% Trogamid-T blend (Figure 7.12). Following the change of T_m^o as a function of the annealing time gives a

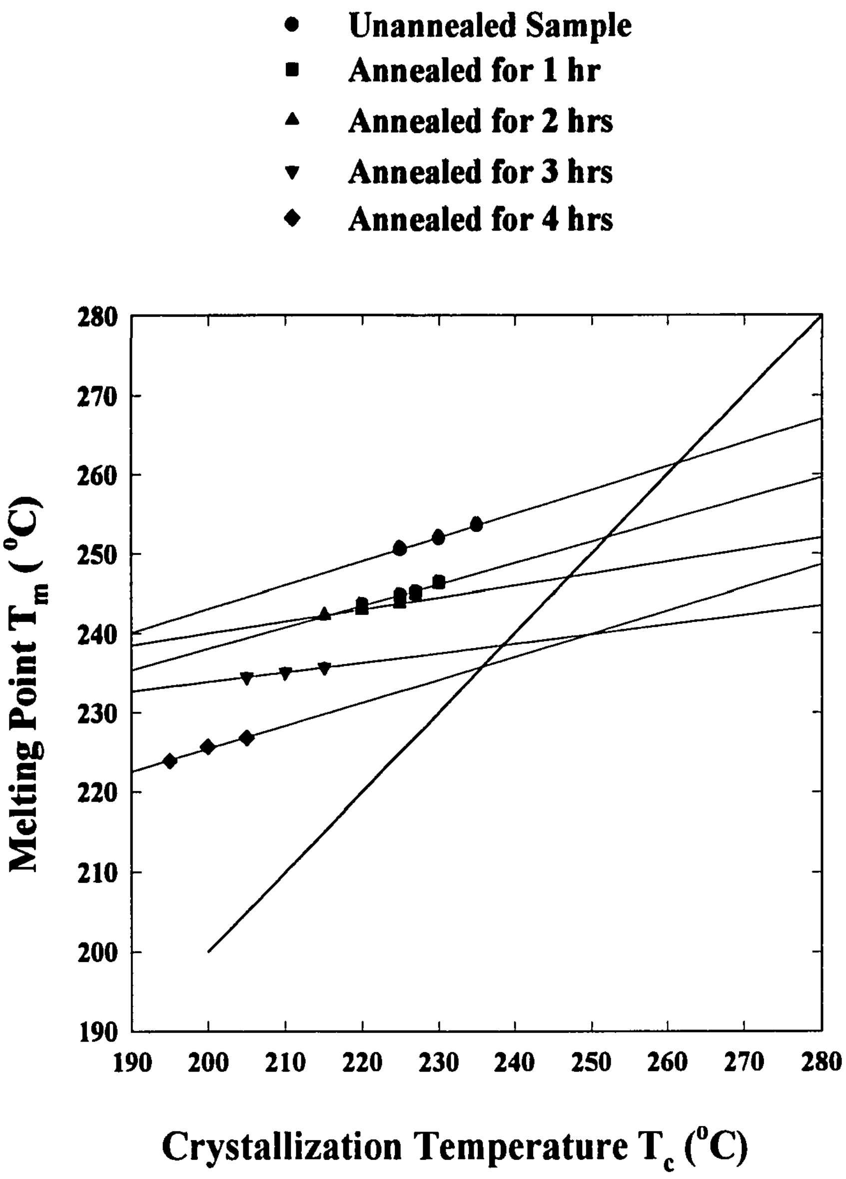


Figure 7.10: Hoffman-Weeks Plots for 10% (RT=5 min) Nylon 6,6/Trogamid-T Blends Annealed for Different Periods of Time

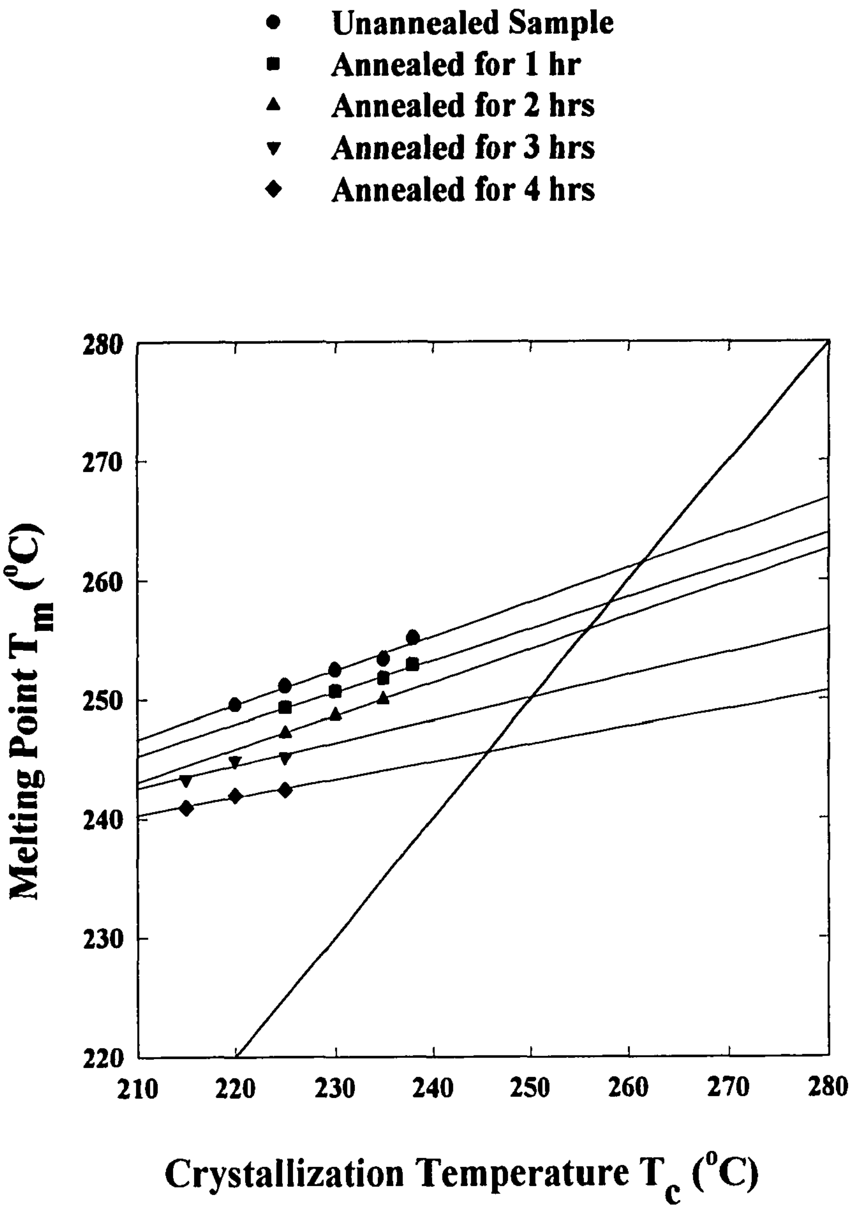


Figure 7.11: Hoffman-Weeks Plots for 10% (RT=5 min) Nylon 6,6/Nylon 6,12 Blends Annealed for Different Periods of Time

quantitative indication of the extent of reaction. As the transamidation reaction proceeds, block copolymers with smaller block lengths are formed, and eventually a true random copolymer results. The T_m^o decreases as the block length decreases with the random copolymer having the least T_m^o. As Figure 7.12 shows, the change of T_m^o is linear with respect to the annealing time, in the time period studied. Takeda et al. [27] reported similar linear behavior of T_m vs. annealing time, for the case of poly(m-xylene adipamide) and nylon 6 blends. However, they did not plot equilibrium melting points but rather the melting point under a heating scan of 20°C/min. The plot showed a curvature at higher annealing times, but a systematic decrease in T_m was observed with increasing residence time. Since both MXD6 and nylon 6 are semi-crystalline polymers, two melting peaks were observed. There was a decrease in T_m of both the polymers and the decrease was linear with respect to annealing temperature. Figure 7.13 shows the same plot for the case of the 10% nylon 6,12 blend and a linear relationship is seen here too. The decrease in T_m^o is less pronounced as compared with the Trogamid-T blend. This is consistent with the previous data, where also the effects were more pronounced for the Trogamid-T blend (non-isothermal and the isothermal data).

7.2.7 Change in T_m^o with Molecular Weight

As discussed in Section 7.1, molecular weight variations were noticed in samples. It is important to determine if this has a significant effect on the melting point of the blends. Flory [40] has derived the following expression relating T_m^o to molecular weight:

$$1/T_m^o - 1/(T_m^o)^{\infty} = 2R/\Delta H_{\mu} X_n \qquad \ldots(5)$$

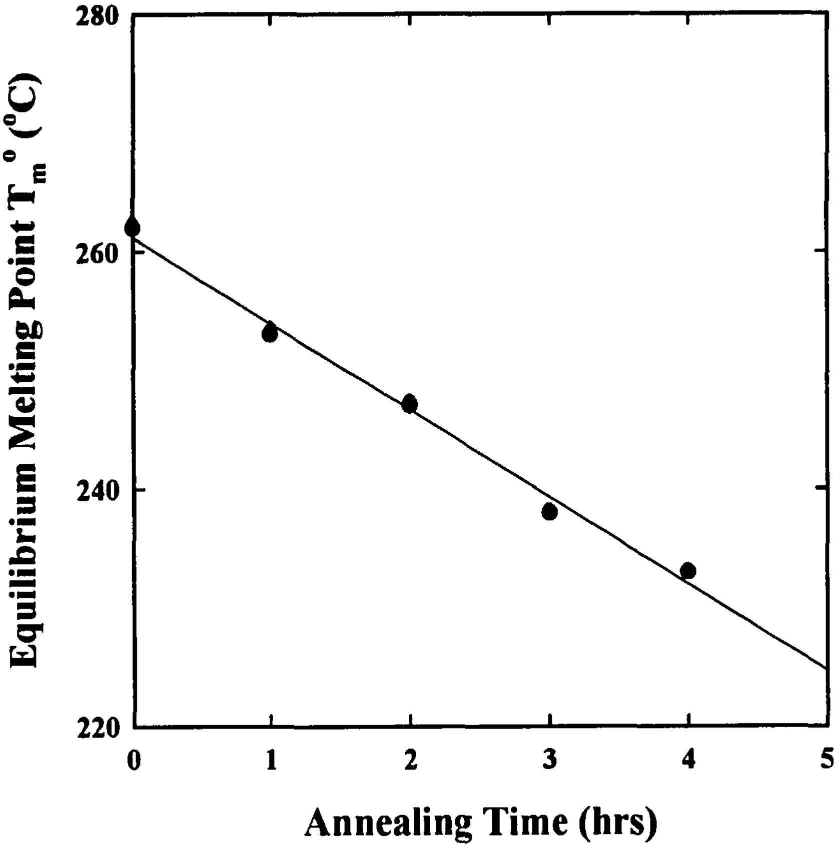


Figure 7.12: Change of T_m^0 as a Function of Annealing Time for a 10% Nylon 6,6/Trogamid-T Blend (RT = 5 min)

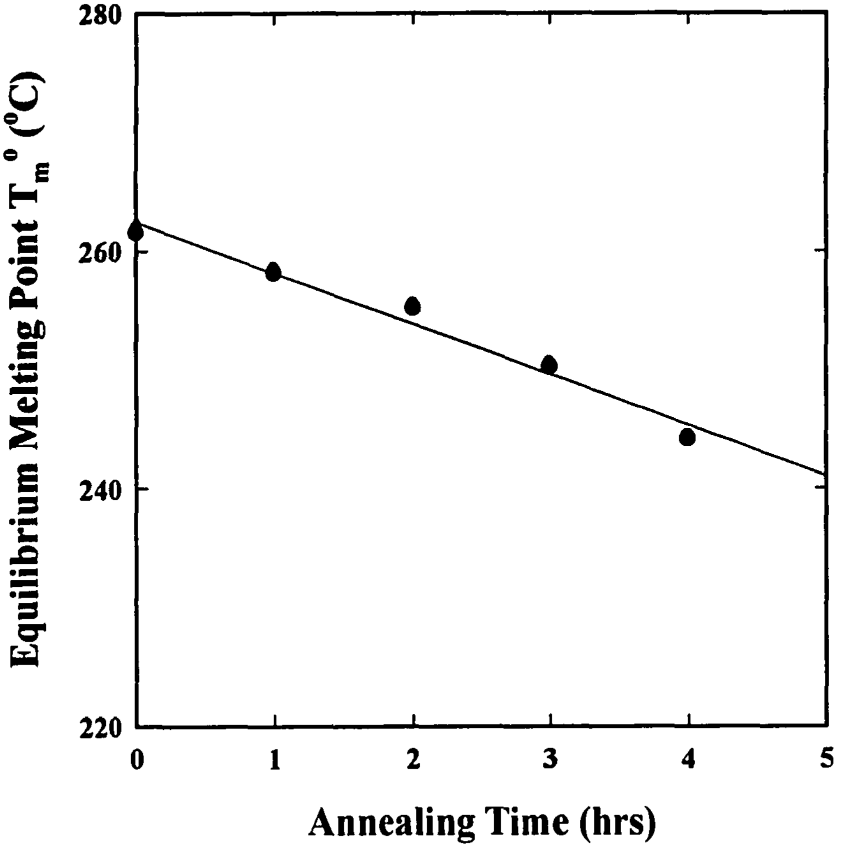


Figure 7.13: Change of T_m^0 as a Function of Annealing Time for a 10% Nylon 6,6/Nylon 6,12 Blend (RT = 5 min)

where T_m^o is the equilibrium melting temperature (in K) for a polymer of number average degree of polymerization X_n, $(T_m^o)^\infty$ is the equilibrium melting temperature (in K) of a polymer of infinite length ($X_n > 100$ for practical purposes), R is the molar gas constant and ΔH_μ is the heat of fusion per mole of repeat unit. Mclaren [5] found this equation to be applicable to nylon 6,6. T_m^o was taken to be 272.5°C and ΔH_μ was estimated to be 4972 cal/mole repeat unit, i.e., per 226 g [5]. Using these vaules, T_m was calculated for molecular weights of 8,000 (X_n=35.9), 15,000 (X_n=67.2) and 30,000 (X_n=134.5). These are shown in Table 7.7.

Table 7.7: Calculated Values for T_m for different molecular weights

M_n	X_n	T_m (°C)
8,000	35.9	266.4
15,000	67.2	269.5
30,000	134.5	271.2

From Table 7.7, it can clearly be seen that the effect of molecular weight on T_m is not very significant. There is only a 4.8°C increase in equilibrium melting temperature on changing the molecular weight fourfold from 8,000 to 30,000. The T_m will not increase on increasing the molecular weight beyond this point. Since the molecular weights of the polymers used in this work are in the 15,000 range, only a 2°C increase in T_m is possible if the molecular weights increase. This can definitely not account for the changes that are being seen in T_m.

In summary, it can be said that an important relationship was established between the extent of interchange reactions and structure of copolymers from the various DSC experiments. The effect of different variables (such as the nature of additive, additive concentration, annealing time, residence time in the extruder and level of mixing) on the extent of reaction was established. This would be helpful in deciding the manner in which copolymers of desired thermal properties can be prepared. By adjusting the additive type and concentration, processing time, and by the use of catalysts, blend systems of the desired thermal properties can possibly be prepared within a range.

7.3 Dynamic Mechanical Thermal Analyzer Runs

Dynamic mechanical measurements were made in the tensile mode, on a Polymer Laboratory Dynamic Mechanical Thermal Analyzer (DMTA). Initial runs at varying frequencies and strains were made with pure nylon 6,6 to determine the optimum conditions to conduct the runs. A frequency of 1 Hz and an extension of 16μm were selected. A temperature scan rate of 5-10°C/min was used. A preset force of 0.55-1.0 N was applied to prevent the sample from buckling during the run. The actual force depended on the sample dimensions. These conditions were used for all runs. In each run, the storage modulus, loss modulus and tanδ, were measured as a function of temperature.

All runs were made done with the Trogamid-T (amorphous) blends since the nylon 6,12 blends revealed no differences in T_g (T_g's of nylon 6,6 and nylon 6,12 are almost identical). Blends of nylon 6,6 and Trogamid-T were observed to be miscible at all concentrations. A single glass transition temperature (T_g) was observed, which decreased with increasing residence time in the extruder. The 5, 10 and 25% nylon 6,6/Trogamid-T blends, with residence times (RT) of 5 min and 30 min in the extruder, were analyzed to check the initial miscibility of the components and the change in miscibility as a function of the reaction time. A typical run is illustrated in Figure 7.14, for the case of the 25% nylon 6,6/Trogamid-T blend with RT=5 min. The loss tangent (tan δ) is plotted against the temperature. The loss tangent is the ratio of storage modulus (G') to the loss modulus (G'') and a peak in the graph indicates a change from the glassy to the rubbery state. Only a single T_g can be observed at 101°C. The T_g for pure Trogamid-T is 153°C (426 K) and close to 65°C (338 K) for pure

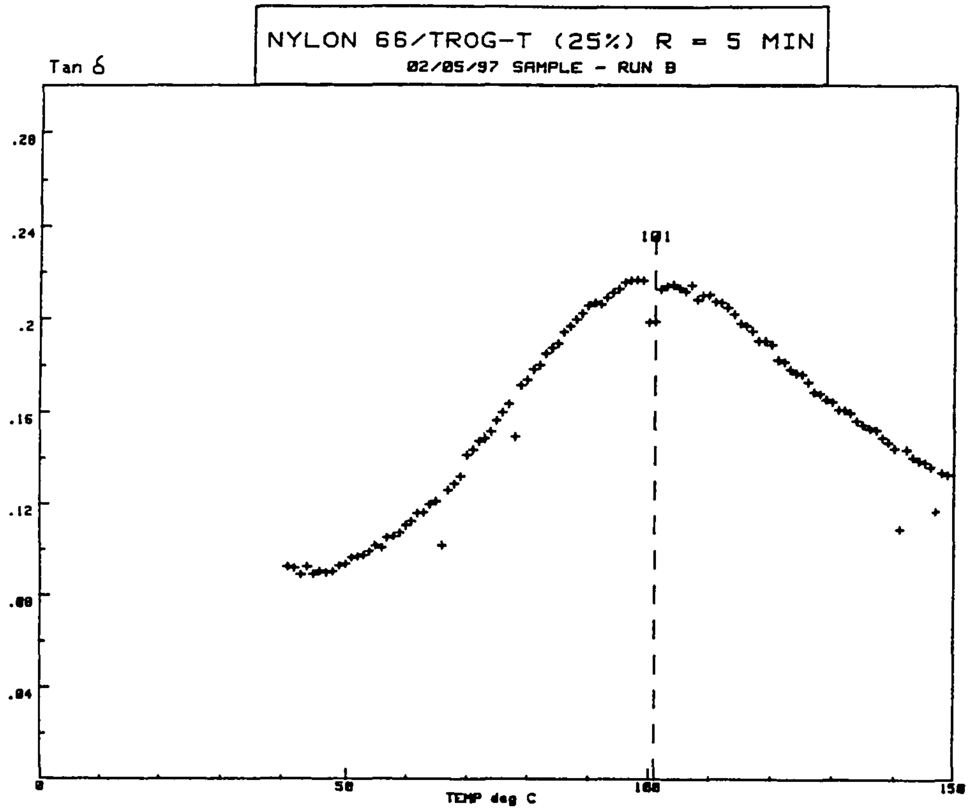


Figure 7.14: DMTA Run for a 25% Nylon 6,6/Trogamid-T Blend with RT=5 min.

nylon 6,6 (depends on the moisture content present). This clearly shows that the as-prepared blend from the extruder yields a miscible blend. Figure 7.15 shows the DMTA run for the 25% nylon 6,6/Trogamid-T blend with RT=30 min. A single T_g can clearly be seen again, at 91.5°C, lower than the previous value, showing that higher residence time leads to a reduction in T_g. This is to be expected since interchange (transamidation) reactions between the components leads to shorter length block copolymers. The decrease in block lengths of the copolymer would invariably result in lowering in T_g due to the increase in mobility of the polymer chain.

Figures 7.16 and 7.17 show the DMTA run for the 10% blends with RT=5 min and 30 min respectively. Figures 7.18 and 7.19 show the DMTA runs for the 5% blends with RT=5 min and 30 min respectively. The results are summarized in Table 7.8. The 10% and 5% blends show similar trends as the 25% blend. A single T_g is observed which decreases with residence time, from 88.5°C to 85.5°C for the 10% blend and from 82°C to 81.5°C for the 5% blend. The degree of suppression (ΔT), defined as the change in T_g between RT=5 and 30 min blends, decreases with decreasing concentration of the blend. This is to be expected since the structure of the copolymers formed is dependent on the concentration of the blends. At higher concentrations more blocks of the aromatic nylon will be incorporated into the nylon 6,6 backbone which will break into smaller blocks as a result of melt annealing. Hence, there is the possibility of more number and distribution of block lengths in the higher concentration blends. This will translate into a larger change in T_g, similar to the higher suppressions in T_c at the higher concentrations.

The T_g of the as-prepared blend increased with increasing blend concentration. This

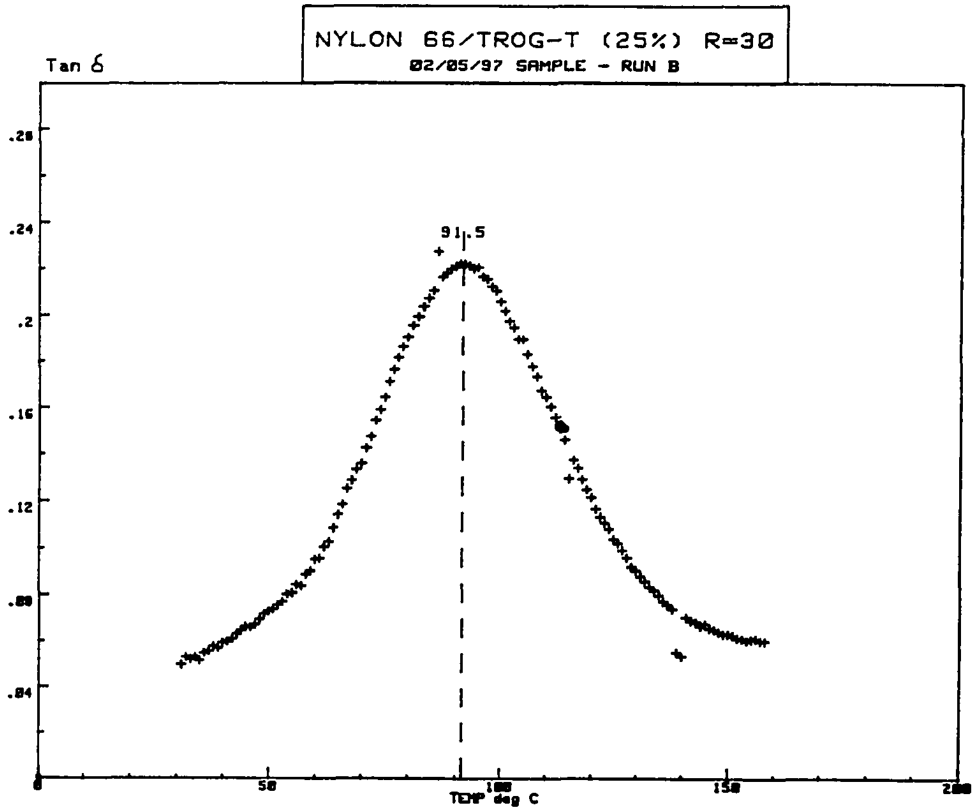


Figure 7.15: DMTA Run for a 25% nylon 6,6/Trogamid-T Blend with RT=30 min.

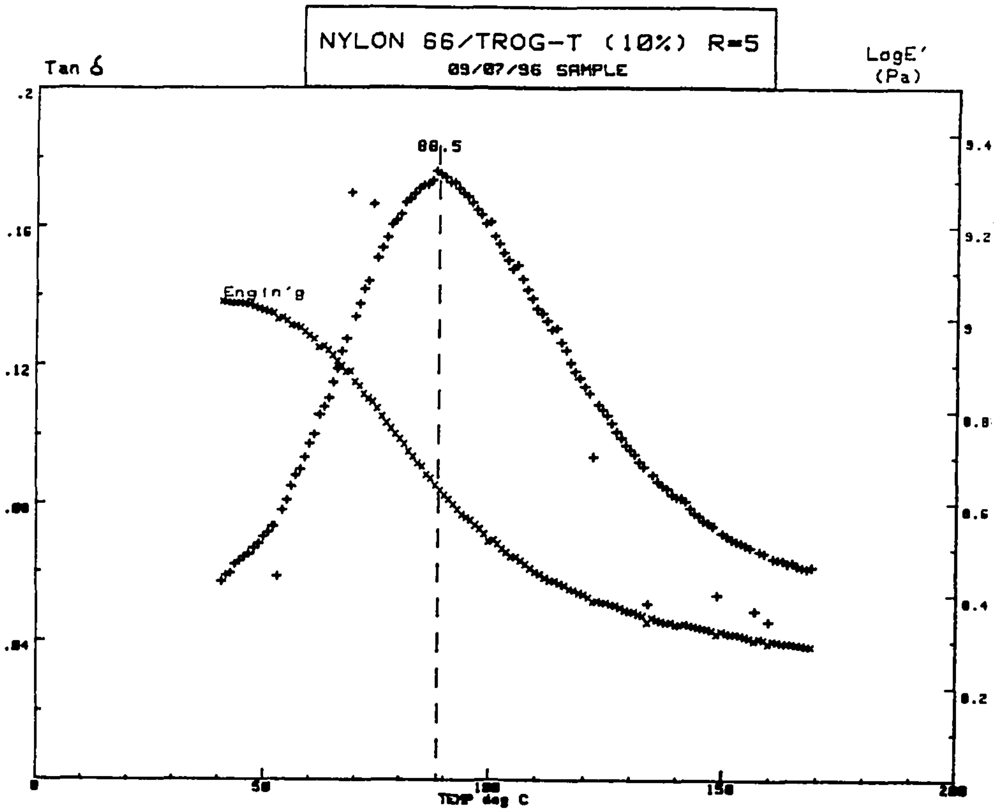


Figure 7.16: DMTA Run for a 10% nylon 6,6/Trogamid-T Blend with RT=5 min.

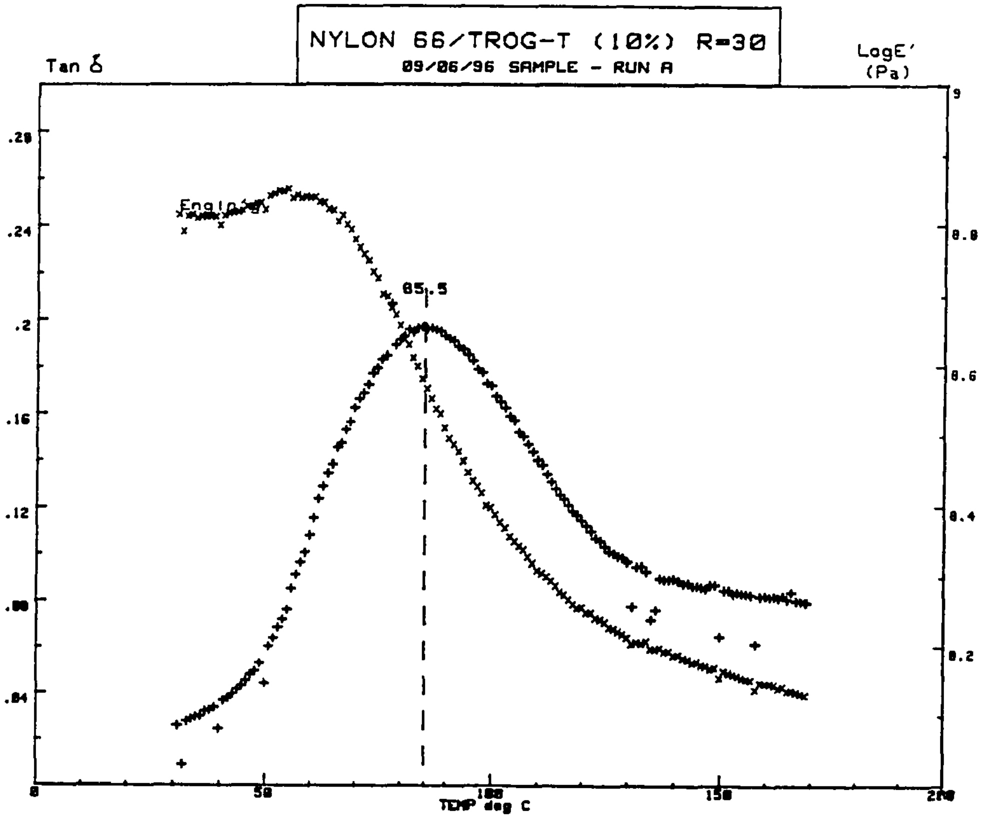


Figure 7.17: DMTA Run for a 10% nylon 6,6/Trogamid-T Blend with RT=30 min.

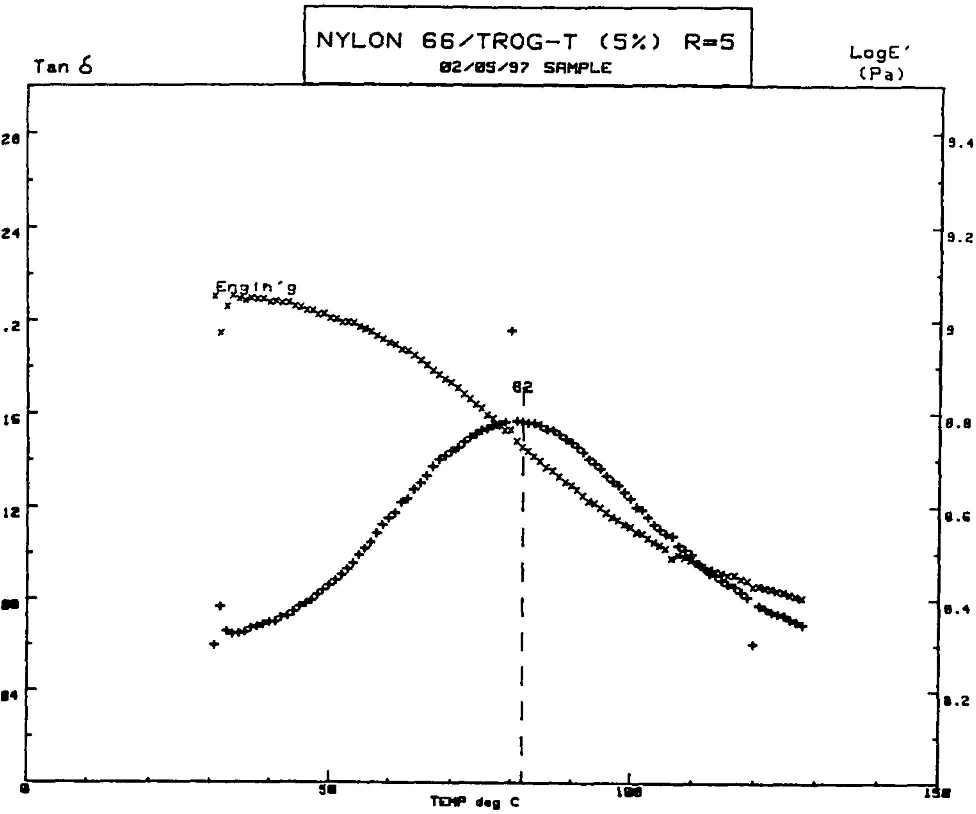


Figure 7.18: DMTA Run for a 5% nylon 6,6/Trogamid-T Blend with RT=5 min

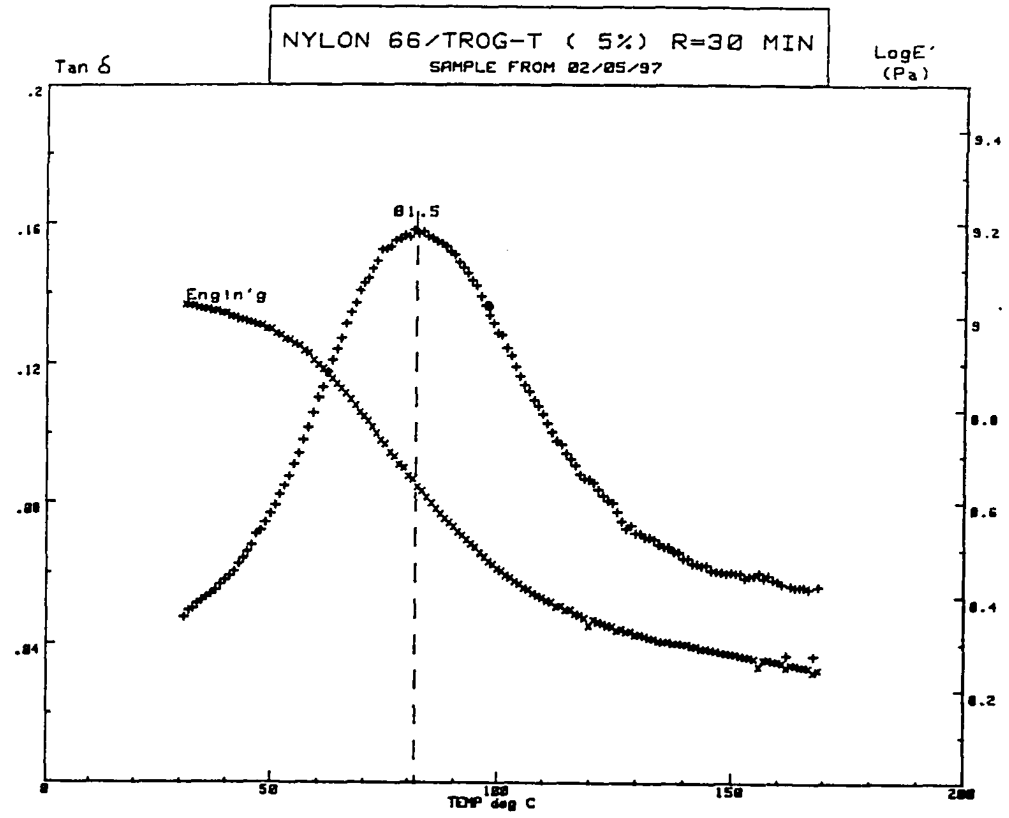


Figure 7.19: DMTA Run for a 5% nylon 6,6/Trogamid-T Blend with RT=30 min.

is consistent, since Trogamid-T has a T_g higher than 6,6. A single composition-dependent T_g intermediate between that of the pure components is a well-known method of detecting miscibility. The data then clearly suggest that the as-prepared blends are completely miscible.

Table 7.8: T_g values of nylon 6,6/Trogamid-T blends (°C)

	RT=5 min	RT=30 min	ΔT^*	Fox T_g	Couchman T_g
25%	101.0	91.5	9.5	92.2	85.5
10%	88.5	85.5	3.0	82.9	80.2
5%	82.0	81.5	0.5	79.9	78.6

*** Degree of suppression**

The T_g of a miscible blend, as a function of composition, can be predicted from the Fox equation:

$$\frac{1}{T_g} = \frac{w_1}{T_{g_1}} + \frac{w_2}{T_{g_2}} \qquad \ldots(6)$$

w_1, w_2: *weight fractions of the components*

T_{g_1}, T_{g_2}: *glass transition temperatures of the components, in K*

This calculated T_g is plotted as a function of concentration in Figure 7.20 and compared with the observed values. It is apparent that the observed T_g is significantly higher than the calculated T_g. Hence, this behavior cannot be predicted simply on miscibility characteristics. The change in T_g as a result of annealing is another indication of the changing chemical structure of the blend. This supports the evidence that interchange reactions are occurring in these blend systems. Takeda et al. [26,27] also reported that the T_g of the mixture (MXD6 and aliphatic nylons) after phase homogenization deviated significantly from the predictions of Eq. 6. Similar positive deviation of T_g with respect to concentration was also noticed by Zimmerman [28], for nylon 6I and MXD-6 blends, and by Eersels et al. [52], for nylon 46 and nylon 6I blends. Similar deviation of T_g has also been reported for physically miscible polyamide/polyamide mixtures [57]. This can be attributed to disruption of short-range order that affects hydrogen bonding, block segment length shortened by interchange reactions, and thermal degradation.

Ellis [56] observed similar composition-dependent single T_g for 3Me6T and nylon 6 blends. He used the theory by Couchman [58] to predict the composition-dependent T_g. Couchman's theory has been used to predict more accurately the behavior of many amorphous polyamide blends and also that of random copolymers. Based on a classical thermodynamic interpretation of the glass transition phenomenon and using the characteristic continuity of entropy through the transition, he derived an expression. Couchman's expression allows the calculation of the T_g of a polymer blend, T_{g12}, using the basic thermal properties of the pure constituents:

$$\ln T_{g12} = \frac{x_1 \Delta C_{p1} \ln T_{g1} + x_2 \Delta C_{p2} \ln T_{g2}}{x_1 \Delta C_{p1} + x_2 \Delta C_{p2}} \qquad \ldots (7)$$

Here x refers to the mass fraction of polymer 1 and 2, respectively, and ΔC_p is the incremental change in heat capacity at T_g of the pure polymer. Using ΔC_p values of 0.827 and 0.39 J g^{-1} K^{-1} [56] for Trogamid-T and nylon 6,6 respectively, T_{g12} was calculated. These values are shown in Table 7.8 and plotted in Figure 7.20, and these lie below the predictions of Eq. 6. Interestingly the T_g-composition curve shows a negative deviation while the experimental data

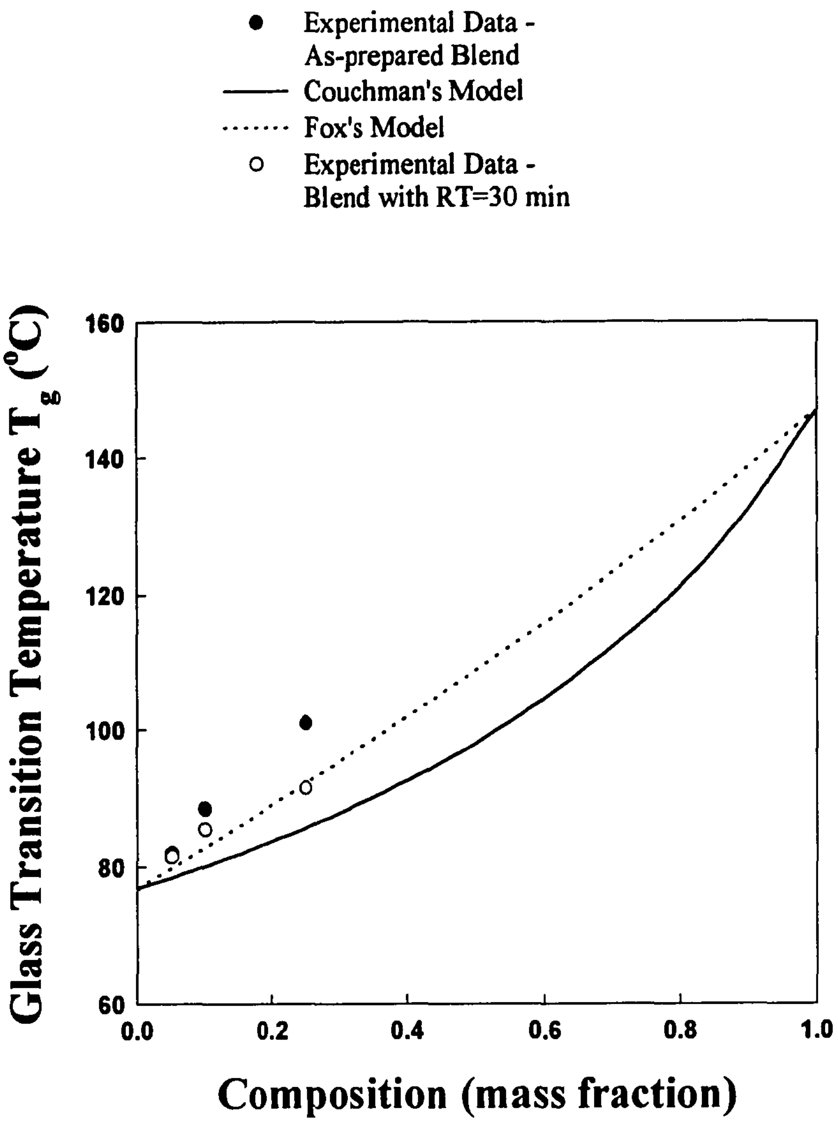


Figure 7.20: T_g versus the Composition Plots of Nylon 6,6/Trogamid-T Blends - Experimental Data, Fox's Model and Couchman's Model

appear to show a positive deviation, providing further proof of better mechanical properties of block copolymers as compared with random copolymers. The deviation, however, does decrease as the sample is annealed in the melt, as the RT=30 min data indicate. It can be expected that the T_g values will decrease with further melt annealing and possibly approach the Couchman curve, which predicts the behavior of random copolymers.

An interesting observation was the occurrence of two glass transitions, at 69.5°C and 108.5°C (Figure 7.21), for the case of a 20% nylon 6,6/Trogamid-T blend prepared earlier on the Maxwell extruder. The Maxwell extruder has poor mixing characteristics and shorter residence time (≈ 2 mins) as compared with the twin screw extruder. Although a single T_g is not visible, some interaction has taken place between the components indicating partial miscibility. The two T_g's are intermediate between the pure component T_g's and appear to be merging. This clearly shows that miscible blends can result with good mixing (higher interfacial area) and with sufficient residence time for reaction to take place. Similar phase homogenization behavior with nylon blends was reported by Takeda and Paul [26,27]. They showed that blends of nylon 6 with poly (m-xylene adipamide), an amorphous aromatic nylon, had two T_g's when prepared by extrusion at 260°C, whereas similar preparation at 290°C yielded a single T_g. The higher temperature was believed to lead to faster interchange reactions and hence the quicker formation of a single phase system. Ellis [56] also observed that miscible blends of nylon 6,6 and MXD-6 were obtained when melt processed for 5 mins.

The blends prepared by Maxwell extruder showed some interaction indicating "near miscibility" which could be expected due to the similarity in structure. Although the residence time is not significantly longer in the TSE (5 min compared to 1-2 min in Maxwell), better

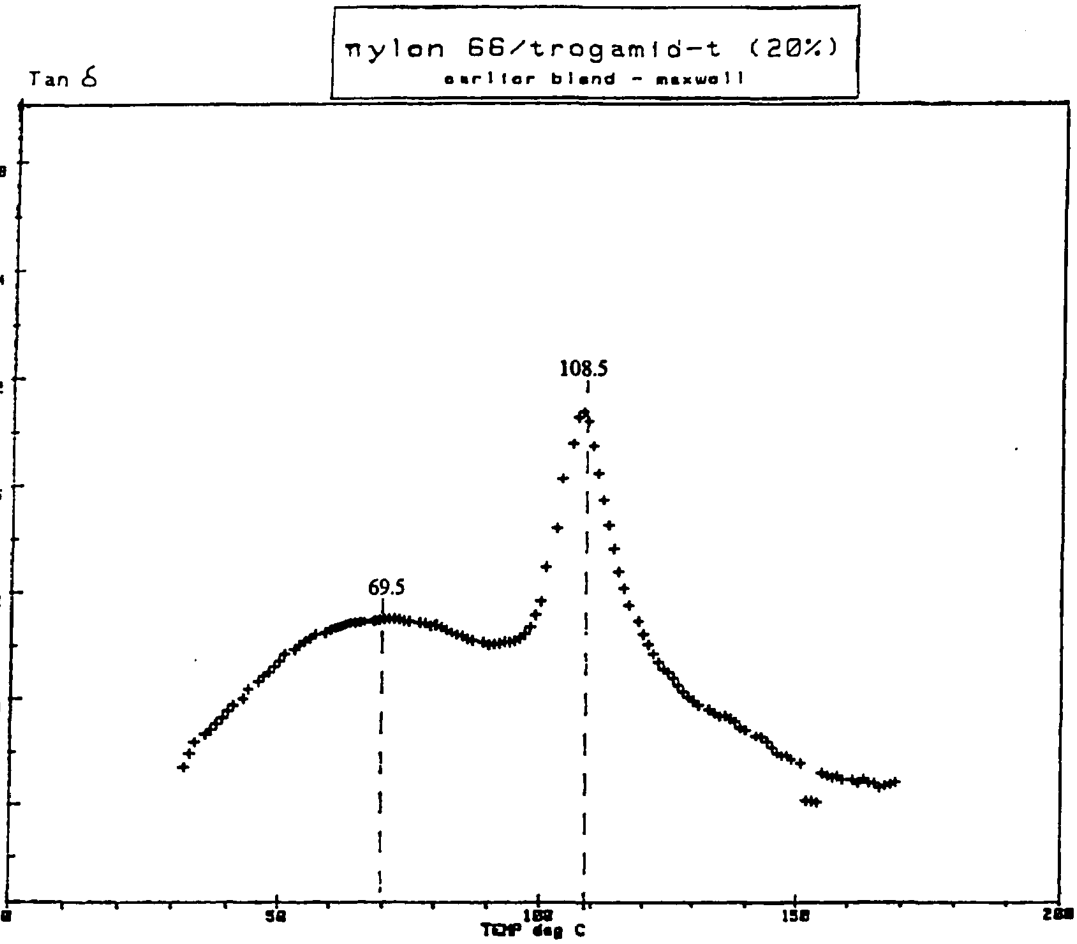


Figure 7.21: DMTA Run for a 20% nylon 6,6/Trogamid-T blend prepared on the Maxwell extruder

mixing in the TSE would produce more initial interfacial area. Hence more reaction would take place in the same amount of time spent in the melt. This could account for the single phase system produced in the TSE (true for different additive concentrations).

Consider the above situation in greater detail [27]. Assume that Trogamid-T forms a dispersed phase of spherical particles (radius R) initially. Then the interfacial area per unit volume, S, is related to R by:

$$S \sim 1/R$$

Based on the principles of fluid breakup (Taylor's theory) [59], correlations for particle size during mixing of polymers have been developed [60,61]:

$$\eta_m RG/\gamma = F(\eta_d/\eta_m) \qquad \ldots (8)$$

where γ is the interfacial tension, G the shear rate, η_m the viscosity of the continuous phase, η_d the viscosity of the dispersed phase. When all variables are considered constant, R is directly proportional to the interfacial tension:

$$R \sim \gamma$$

However, a lower R will result in flow fields with higher shear rate G, which is the case with the twin screw extruder.

Mean-field theories [62,63] and available experimental evidence [64,65] suggest that the polymer-polymer interface is diffuse and can be characterized by a thickness λ. Theory of Helfand and coworkers [62,63] gives:

$$\gamma = (kT/a)(m\chi)^{1/2} \text{ or } \gamma \sim \chi^{1/2} \qquad \ldots (9)$$

$$\lambda = 2(m\chi)^{-1/2} \text{ or } \lambda \sim \chi^{-1/2} \qquad \ldots (10)$$

where m and a are physical parameters and χ is the Flory-Huggins interaction parameter.

When the polymer-polymer interaction is more unfavorable, the interfacial contact will be less and the interfacial compositional gradient will be sharper, i.e., less mixing per unit area of contact.

The volume of the interfacial zone occupied by the mixed polymers is proportional to the product of S and λ.

$$S\lambda \sim \lambda/R \sim \lambda/\gamma \qquad \ldots(11)$$

Hence:

$$S\lambda \sim 1/\chi$$

As the interaction energy becomes less positive or favorable for mixing, the interfacial volume where interchange reactions can occur, increases. Reaction leads to the formation of copolymer which further decreases the interfacial tension and therefore increases the interfacial volume. Hence, the opportunity for further reaction will improve.

As far as nylon 6,6/nylon 6,12 blends are concerned, miscibility could not be studied due to the almost identical T_g's exhibited by the pure components. Recent work by Ellis [66] with aliphatic nylon blends has shown nylon 6,6 and nylon 6,12 blends to be immiscible. He used enthalpic recovery measurements [67] in modulated DSC experiments to measure the miscibility of the blend. His model (discussed in Appendix D) also predicts all aliphatic nylon blends to be immiscible. It was found that the blends of various aliphatic polyamides with 3Me6T showed a clear correlation between miscibility and the concentration of methylene units of the aliphatic polyamides. Nylon 3Me6T was found to be soluble in nylons 6, 66, 69, 610, and 612 but insoluble in nylons 4, 46, 11, and 12. Nylon 6,6 is predicted to be completely miscible with this amorphous nylon and this has been observed experimentally too

[67]. The effective interaction parameter χ_{blend} value for Trogamid-T and nylon 6 (or nylon 6,6) was negative but very small in magnitude. Ellis prepared nylon 6/Trogamid-T blends by precipitation from 98% formic acid. Hence, there would be lower heat treatment during the solvent removal step. However, the T_g was determined from DSC quench samples, which invariably involves heating the sample to melt temperatures. As discussed earlier, the solution blends were observed to be more reactive and it is possible that even a small exposure to molten conditions could have initiated enough reaction to produce miscible blends. In our case, DMTA was used for T_g measurements and there was no exposure to melt conditions (except in the preparation of the film samples).

It can be concluded that nylon 6,6/Trogamid-T blends are not miscible in the absence of reactions, although they appear to be close to miscibility. This is contrary, both to experimental observations and theoretical predictions of Ellis. However, Ellis predicted the blend to be miscible by a small degree (small negative χ_{blend}). It would appear that this blend, in reality, has a very small positive χ_{blend}. Hence, only a small degree of interchange reaction leads to the formation of a miscible blend. Finally it can be said that the miscibility of nylon 6,6 and Trogamid-T blends was clearly established. It was shown that this blend system was "nearly miscible" and only a small extent of reaction was needed to produce miscible blends at all concentrations. Nylon 6,12 blends appeared to become miscible (as discussed in Chapter 7.2.2), although at much longer melt annealing times. The importance of interchange reactions in promoting miscibility was also shown. There is great potential of using these reactions for improving physical properties of immiscible blends. Though reaching miscibility in some cases might be difficult, due to the large extent of reaction required, compatibility can certainly be improved, even at small extents of reaction. The fact that interchange reactions promote miscibility which increases “reaction volume” and promotes further reactions, is a very fortunate situation. The formation of miscible blends of nylon 6,6/Trogamid-T during the extrusion process, is an important observation from a commercial viewpoint, both in terms of the mechanical and thermal properties of the blend.

7.4 Optical Microscopy Results

Polarized microscopy allows for the visual study of the growth of the spherulites. This technique was investigated to compare the spherulitic growth rate of nylon 6,6 with the blends and the change in morphology of the spherulites (number, size and shape). However, the spherulites could not be successfully viewed with this technique. Thin films (~20 to 30 μm) had to be used to allow for the proper focussing on the spherulites. With the thin films, however, large spherulites were not observed. Instead a granular birefringent texture was observed, with spherulites too small (less than 2 μm) to be viewed clearly. Hence, following the growth of the spherulites was impossible. This type of granular texture has been attributed to “transcrystalline spherulitic brushes”[1]. These structures have been observed in thin films and have been attributed to localization of nuclei that greatly distort spherulitic growth. X-ray measurements [1] have shown that these structures consist of closely spaced layers of radial sections of spherulites resulting from numerous nucleation sites at the surface.

Many factors could be responsible for the formation of these structures. Generally faster rate of crystallization has been observed in thin films [5]. This was attributed to surface nucleation, more efficient dissipation of the heat of crystallization, and near two-dimensional growth in thin films. It was also suggested that in thin films there was evidence of both primary and secondary nucleation. Mclaren [5] also observed that with high molecular weights (> 15,000), unsatisfactory films were obtained, with a considerable amount of fine granular birefringent material. It was thought that the high melt viscosities of these higher molecular weight polymers modify the flow properties of the films and cause strain. The strain could then induce crystallization. Presence of impurities can also enhance nucleation and lead to the formation of large number of small spherulites, which would give the granular texture. The use of clean samples did not solve the above problem. It should be noted that the Rhodia nylon 6,6 has titanium dioxide which can act as a possible nucleant [4]. However, specimens prepared from Dupont and SPP nylon 6,6 did not show increased spherulitic size. The nature of additives in these nylons is not known but they are expected to have relatively less additives. Magill [4] also observed variations of spherulitic size within the sample, with portions of the sample having completely granular background. Such variations were also present with our samples.

It did appear that surface of the cover slides was influencing the crystallization behavior. There was the presence of larger spherulites around the edges of water bubbles present in undried polymer samples. The surface tension of the water bubbles could alter the nucleation process. It did appear that enhanced nucleation was producing the granular background but the exact cause could not be determined.

However, polarized microscopy studies did confirm the decrease in T_c of the blends. No birefringence was developed when the blend samples were held isothermal at high temperatures (230 - 250°C) even after long periods of time (~1 hr). Pure nylon 6,6 did develop birefringence and consequently a spherulitic structure under the same isothermal temperatures. This merely supports the DSC data showing reductions in T_c of the as-prepared and annealed blend samples, without providing any additional information.

7.5 Summary and Discussion

The primary objective of this work was to find the means of reducing the crystallization rate of nylon 6,6 using polymeric additives and to explain the mechanism of additive action. This was with a view to control and improve polymer physical properties. Blends of nylon 6,6 with a number of commercially available polymers showed that only small suppressions in T_c could be obtained with "physical blends", i.e., blends where there is no reaction between the components. This was in accord with the effects predicted from theory (small changes in T_c and no changes in the total level of crystallinity). In contrast, reactive blends showed significant reductions in the rate of crystallization (as indicated by T_c) and the amount of crystallization (ΔH_c), depending on the extent of reaction. Although interchange (transamidation) reactions between nylons were studied in-depth, other polymers capable of reacting with nylon 6,6 were also investigated.

In the initial screening experiments, a number of additives were either solution or melt blended with nylon 6,6. The effect of blending on the thermal behavior of nylon 6,6 was studied primarily by non-isothermal DSC experiments. All the amorphous polymers, nylon 6(3) T, Trogamid-T, Zytel 330, polycarbonate, polyphenylene ether and polyacrylic acid, having a T_g higher than nylon 6,6, caused a decrease in the T_c. The reductions were of the order of 5-15°C. Polyacrylic acid and Trogamid-T produced the largest effect, followed by

Zytel 330. Since polyacrylic acid was solution blended and could not be melt blended (it was not processable at the melt temperatures of nylon 6,6), further work was restricted to Trogamid-T. The reason for the reduction in T_c with the amorphous polymers was attributed to the increase in blend T_g and slower diffusion. Since the additive has a higher T_g than nylon 6,6, a miscible blend would have an increased T_g as well as a slight depression in T_m. This would suppress the temperature range of crystallization of (T_g - T_m). A higher blend T_g signifies lower chain mobility at a given crystallization temperature and hence causes slower diffusion rates and lower spherulitic growth rates. In addition, the presence of the amorphous additive in the path of the growing crystal front would also slow the crystallization process.

Trogamid-T was "nearly miscible" with nylon 6,6 and Zytel 330 was close to miscibility and hence the above effects would explain the reduction in T_c. The miscibility of the other additives with nylon 6,6 was not investigated. However, it should be noted that even if immiscible blends were formed with these additives, slower crystallization can still result. In this case, the amorphous additive would be dispersed in the melt as droplets. The size of the droplets would depend on the extent of incompatibility of the polymers and the blending conditions. These droplets will be rejected, occluded or deformed by the growing spherulites, slowing the crystallization process.

Blends with the semi-crystalline blends also showed decrease in T_c, but the effects, as with the amorphous additives, were not significant. The additives tried included nylon 6,12, nylon 12, nylon 6, polymethyl methacrylate, polyacrylamide, Exxelor PO1015 and polyethylene oxide. Nylon 6,12 blends showed the most effect on the thermal behavior. Surprisingly the T_c, T_m, and heats of fusion and crystallization, decreased progressively in successive DSC runs. It was concluded that the two nylons were reacting and this was causing the change in the thermal behavior of the blends. The reaction was as a result of annealing in the melt.

At this stage the other blends were annealed in the melt for different periods of time to see the effect of reaction on these blends. It was found that significant changes in thermal behavior could be produced as a result of annealing in the melt. These changes were significanlty more than that encountered with the "physical blends". The changes in thermal behavior were a function of the time of annealing, additive concentration and the nature of the additive. All nylon blends showed changes in thermal behavior due to the possibility of interchange reactions between nylons. The known reaction mechanisms are acidolysis, aminolysis and amidolysis. All the above reactions are expected to lead to the formation of block copolymers initially and random copolymers finally. Literature shows block copolymers to have better mechanical properties when compared with random copolymers and hence block copolymers are to be preferred. Since nylons have an acid and an amine end group and amide linkages in the backbone, there was a possibility of reaction with polymers containing appropriate end groups. Detailed experimentation to understand the interchange reactions was conducted with nylon 6,12 and Trogamid-T blends.

In general, these reactions were observed to be very slow, especially at low concentrations of the additive. Very high annealing times (~ 4 hrs) are required for producing significant thermal changes. This would be unattractive from a commercial viewpoint, since low additive concentrations are desired. However, it was shown that these reactions can be promoted by using a catalyst (triphenyl phosphite). Although the mechanism of the catalyst action is unknown and there are practical difficulties in the introduction of the catalyst into the blend, this has the potential for solving the problem of high melt annealing times.

As expected, Trogamid-T blends showed larger effects as compared with nylon 6,12 blends. The decrease in T_c was more and the isothermal crystallization times were longer, at the same concentration and annealing times. This was attributed to nature of block copolymers formed during the process of melt annealing. The block copolymers with Trogamid-T will have non-crystallizable segments built into the polymer. In comparison, nylon 6,12 blends will have crystallizable segments built in, although of a different structure and inherent crystallizibility. Hence, the effect on the rate of crystallization is to be expected to be higher for Trogamid-T.

There was negligible effect of higher residence time in the extruder, on the thermal properties of Trogamid-T blends, which were found to be miscible and hence interchange reactions will not be promoted by additional shearing. Miscibility with nylon 6,12 was not studied (due to analytical limitations). However, there was an effect of higher residence time on the extent of reaction and hence the thermal behavior of the blends, suggesting initial immiscibility. DSC experiments showed that the nylon 6,12 melting peak disappeared with a small amount of melt annealing (~ 10 min). If all the nylon 6,12 is getting incorporated into copolymers, the absence of any phase boundaries is a reasonable conclusion. Hence nylon 6,12 blends are expected to become miscible with only small melt annealing times.

DMTA experiments showed that Trogamid-T blends to be miscible at all concentrations. Surprisingly, blends made on the Maxwell extruder showed two T_g's while blends prepared on the twin screw extruder showed a single T_g. Thus Trogamid-T blends were initially immiscible but became miscible with a small amount of reaction, suggesting "near miscibility". The T_g versus the composition curve showed positive deviation from linear additivity. The composition-dependent single T_g decreased as a function of annealing time. The change in T_g as a result of annealing is another indication of the changing chemical structure of the blend. The decrease in block lengths of the copolymer would invariably result in decrease in T_g due to the increase in mobility of the polymer chain.

Although the formation of block/random copolymers was not confirmed directly in this work, all the observations strongly support the formation of such copolymers. The results obtained are consistent with the observations made by other workers [26-28, 52-55] and provide further proof of interchange reactions. Since the block copolymers are known to have better physical properties, as compared with the homopolymers and the random copolymer, this has additional commercial attraction. There is a possibility of making blends miscible, with improved morphology and properties. The positive influence of interchange reactions on T_g (and hence modulus) is another indication of better properties. Additionally, the extent of these reactions can be controlled by the additive type and concentration, reaction time (and temperature), and by the use of catalysts (or inhibitors). Hence, the properties of the blend can be controlled with controlled reactions leading to the desired concentration of block copolymers.

Finally it can be said that the objectives of this work were successfully met. Additives were identified that reduced the rate and degree of crystallization in nylon 6,6. The mechanism of additive action was verified and the effect of different variables was studied. It is believed that the block copolymers have improved physical properties. Synergistic improvements in glass transition were seen. Hence, a method (reactive blending) has been developed by which the mechanical properties of nylon 6,6 (and possibly other nylons or other types of polymers) can be improved directly as well as indirectly via the crystalline structure. In addition a potential method of producing miscibility (or enhancing compatibility), with obvious commercial interest, was identified.

CHAPTER 8

CONCLUSIONS & RECOMMENDATIONS FOR FUTURE WORK

The following conclusions can be drawn from this research work:

- Annealing polyamide blends in the melt results in interchange reactions.

- Interchange reactions produce copolymers with reduced T_c, T_m and heats of fusion and crystallization. Hence there is a decrease in the rate and the degree of crystallization.

- The changes in thermal behavior depend on the nature and concentration of additive and the melt annealing time.

- Blending method (solution or melt) has a pronounced effect on the initial thermal properties as well as the rate of change of these properties. This is related to the extent of mixing of the blend components.

- Additional shearing (higher residence time in the extruder) promotes the interchange reactions in immiscible or partially miscible blends.

- Interchange reactions increase miscibility via the emulsifying effects of the copolymers. The time required to produce miscible blends is related to the initial miscibility and the extent of reaction. Trogamid-T blends were "nearly miscible" and miscible blends were produced on the TSE. Only a small degree of reaction was needed for miscibility. In contrast, nylon 6,12 blends appeared to be immiscible and longer times (less than 10 mins) were needed to possibly produce miscible blends.

- Trogamid-T blends produced larger effects on the thermal behavior of nylon 6,6 as compared with nylon 6,12. This was attributed to the incorporation of non-crystallizable segments of Trogamid-T into the crystalline nylon 6,6 structure.

- Reactive extrusion is a feasible method to change the properties (mechanical and thermal) with the proper choice of additive and the extent of reaction (controlled by the additive concentration, reaction time and miscibility). This work showed that blends with reduced rates and degree of crystallinity as well as reduced T_m can be prepared. It is possible, for example, to prepare blends with increased T_g and T_m with copolymers of nylon 6,6 and nylon 6,T [68] with reduced rates of crystallization. Contrary to most copolymer systems, nylon 6,6/nylon 6,T copolymers show increase in T_m compared with the T_m of pure nylon 6,6, due to co-crystallization of the isomorphous crystalline units [69]. However, both the rate of crystallization and the degree of crystallinity are reduced due to the diluent effect of nylon 6T units in the nylon 6,6 crystalline areas.

This work conclusively showed the effect of interchange reaction on the thermal behavior of nylon 6,6. Reaction was indirectly measured through the depression in T_m. However, no direct evidence of reaction or the formation of copolymers was provided. It is important to have a better insight into the change of molecular structure as a result of interchange reactions in order to understand the final properties. A change in molecular structure will change the physical properties. Also the morphology of the polymer will change, leading to changes in final properties of the blend. In polyamide blends composed of a semicrystalline aliphatic polyamide and an amorphous aromatic polyamide, the knowledge of the block length of the homogeneous blocks of the aliphatic polyamide can give information about the kinetics and the ability of crystallization [53]. Techniques to study structure, such as IR, are not applicable for these systems because of the similarity in structure. Hence it is recommended that a NMR technique should be developed to directly identify and measure the amount of copolymer formed. Such work has been recently conducted by Eersels et al. [52-55] with blends of nylon 46 and nylon 6I. The ^{13}C NMR technique allows for the determination of the degree of randomness and the number-average block length of the copolymers and is reported to be more accurate than proton NMR.

The intrinsic viscosity work could not provide conclusively evidence about the changes in molecular weights due to interchange reactions. This was due to the batch method of preparing the blends, especially with the longer residence time blends. Hence, it is recommended to prepare blends with continuous extrusion. This can be achieved by using batch mixers or if twin screw extruder had to be used, by using smaller dies that would increase the residence time in the extruder. Some work with smaller dies was done and a problem with high pressure development was noticed, leading to blockage and leakage of material from the sides of the extruder. This problem would have to be tackled before continuous extrusion with high residence time can be done. In addition, continuous extrusion with undried material should be carried out to provide conditions leading to a reduction in molecular weight. This could provide very useful information about the effect of reaction on molecular weight and hence, possibly, the mechanism of reaction.

Further, a vacuum oven, capable of operating at high temperatures (upto 400°C) could be constructed. The vacuum oven presently available can reach 300°C but only partial melting is observed under these conditions of vacuum. The availability of such a setup would allow one to see the effect of annealing (reaction) under devolatizing conditions, without the problem of degradation and fluctuations in properties. This would also eliminate the need for using the twin screw extruder to melt anneal samples. In addition, by using different vacuum conditions, the effect of the rate of water removal can also be studied.

Difficulties were encountered in the measurement of molecular weights, both with the intrinsic viscosity method and because of possible fluctuations in the blend sample. It will be worthwhile to develop a method to measure the molecular weight distribution (such as elution gradient chromatography). However, since nylons are only soluble in highly polar (and expensive) solvents, this is a potential problem. Eersels and Groeninckx [70] reported the use of such a method for the case of nylon 46 and nylon 6I blends.

The miscibility of aliphatic nylons with nylon 6,6 could not be studied due to the proximity of the T_g's. The conventional DSC cannot resolve between the two transitions. However, modulated DSC allows such resolution. The peak in the enthalpic relaxation experiments can be used to detect the glass transition of the blend. Such work has been carried out recently by Ellis [71]. The use of a modulated DSC module will allow one to study miscibility in aliphatic nylon blends.

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APPENDIX A

RUNS FOR SCREENING EXPERIMENTS

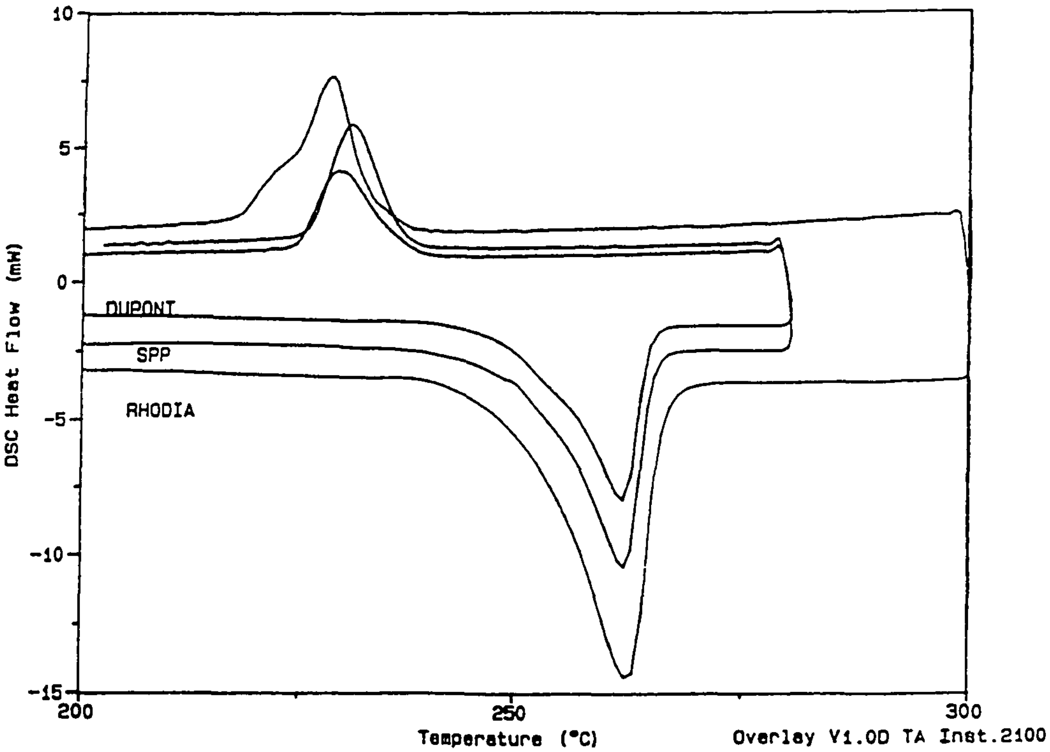


FIGURE A.1: Heating (10°C/min) and Cooling Runs For Nylon 6,6 from Rhodia Inc., Dupont and Scientific Polymer Products

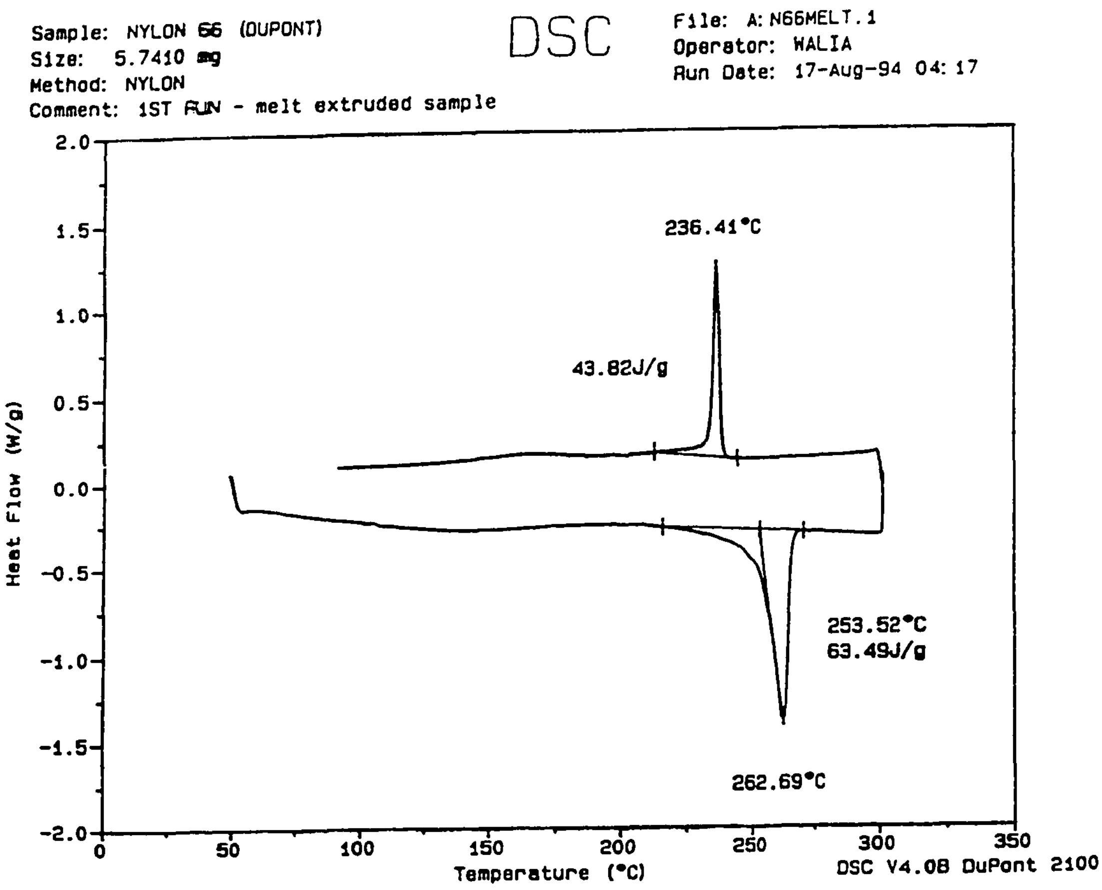


FIGURE A.2: DSC Thermogram for Melt Extruded Nylon 6,6 (Zytel 101, Dupont)

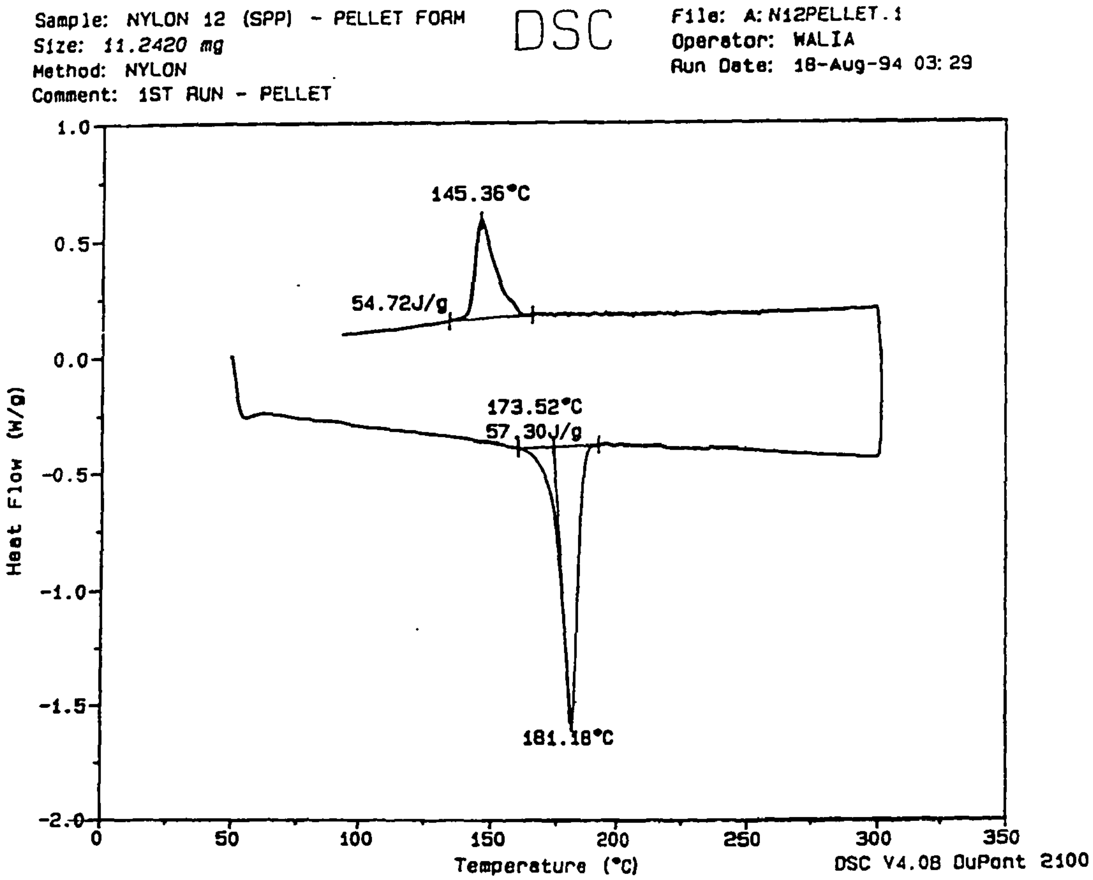


FIGURE A.3: DSC Run for Nylon 12 Pellet

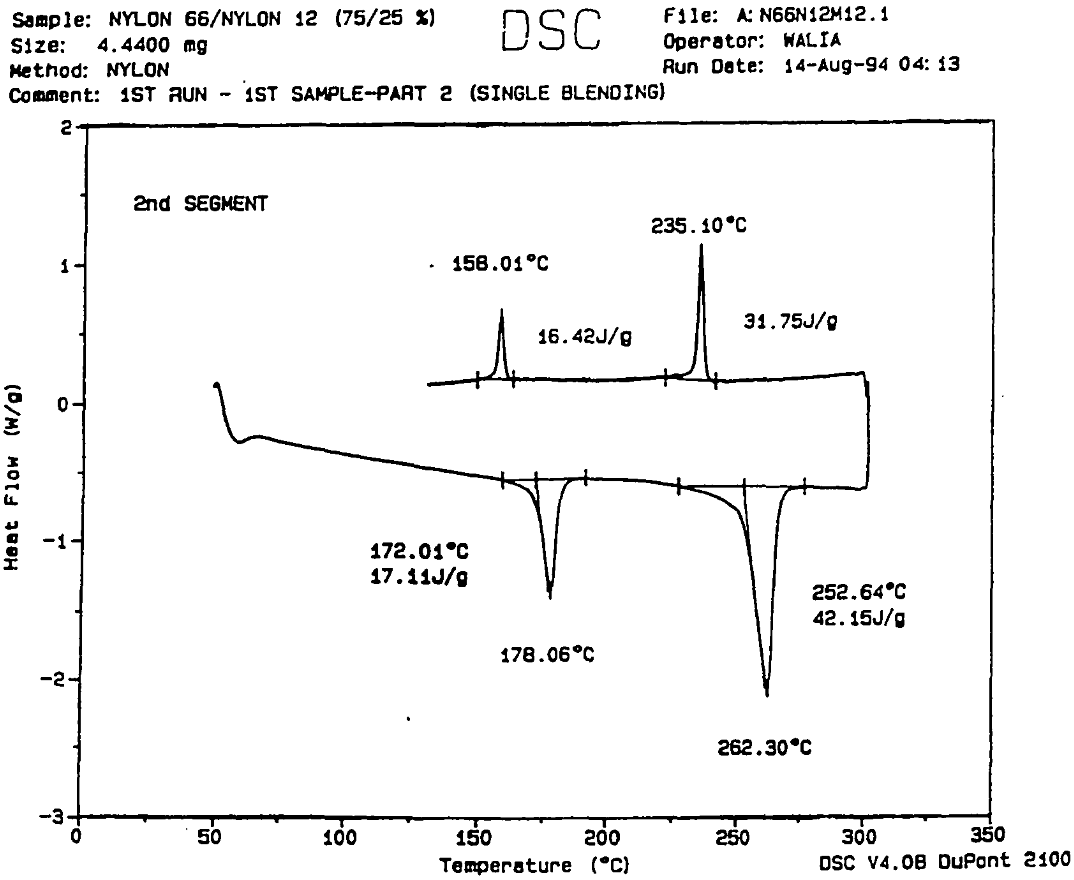


FIGURE A.4: DSC First Run for a Nylon 6,6/Nylon 12 (75/25% wt/wt) Blend - First Sample

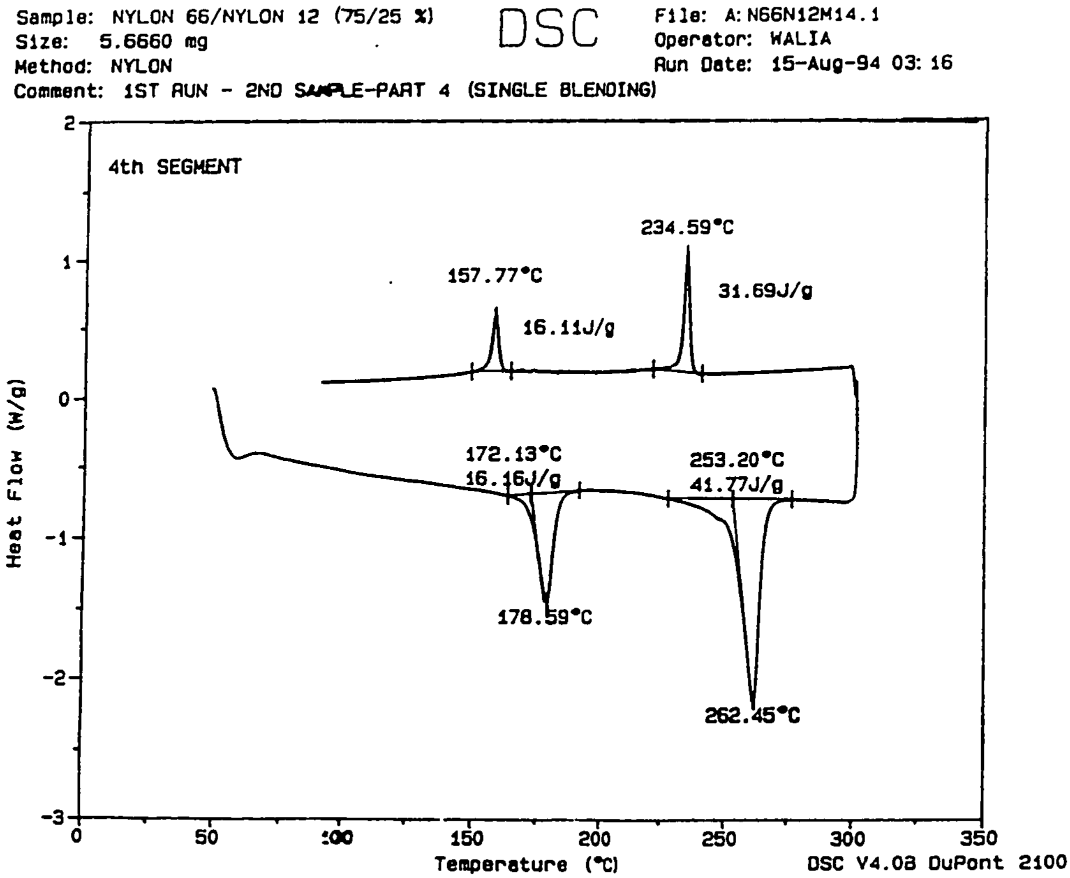


FIGURE A.5: DSC First Run for a Nylon 6,6/Nylon 12 (75/25% wt/wt) Blend- Second Sample

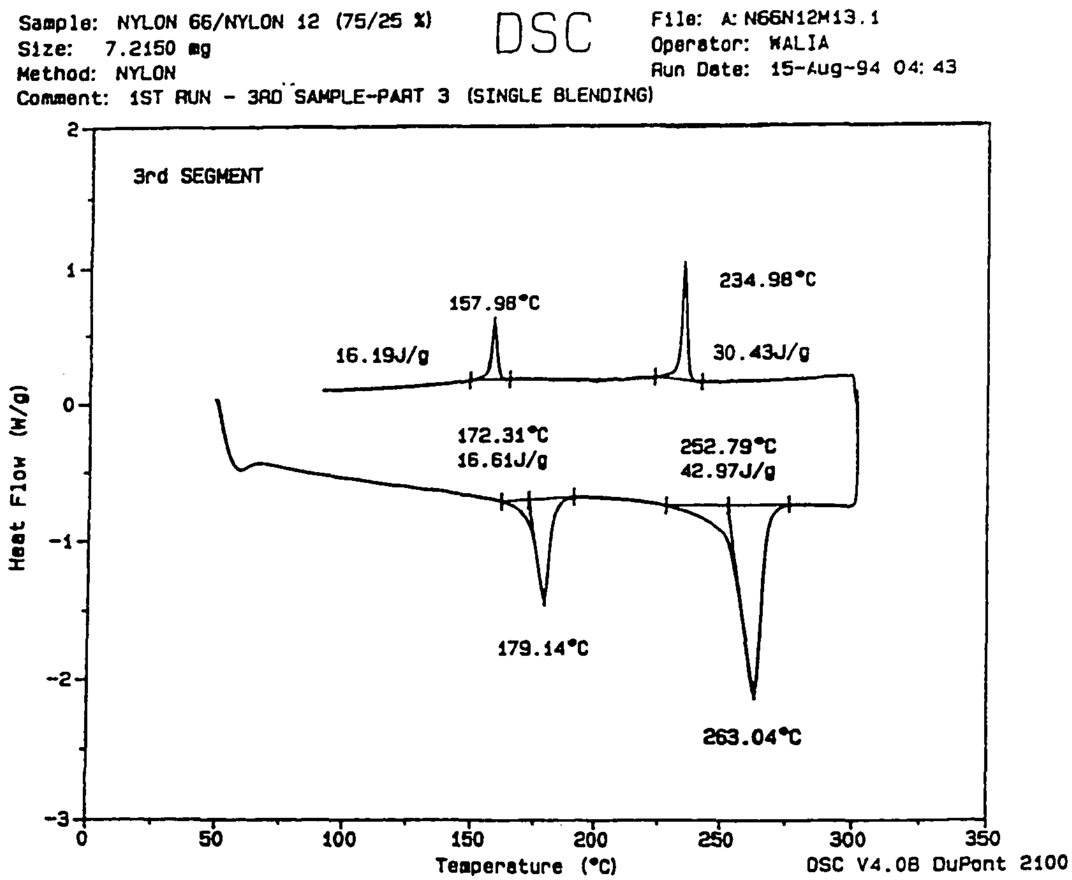


FIGURE A.6: DSC First Run for a Nylon 6,6/Nylon 12 (75/25% wt/wt) Blend - Third Sample

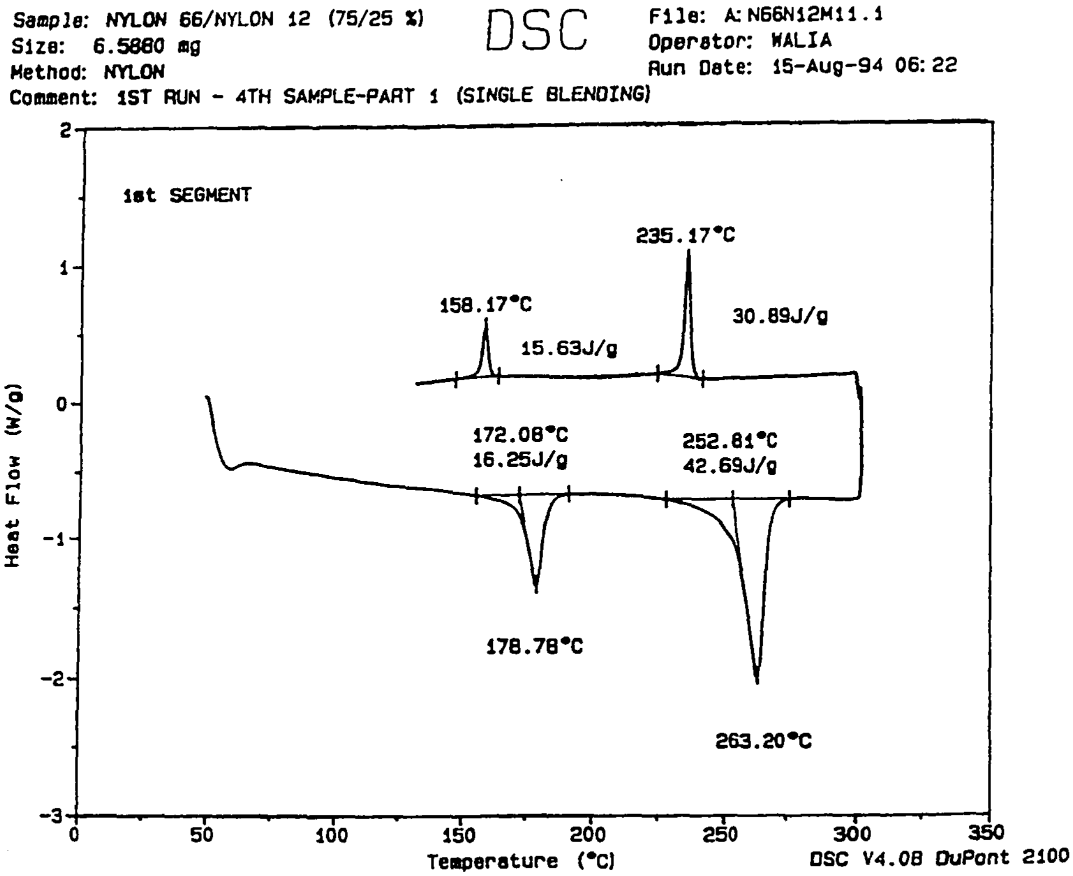


FIGURE A.7: DSC First Run for a Nylon 6,6/Nylon 12 (75/25% wt/wt) Blend - Fourth Sample

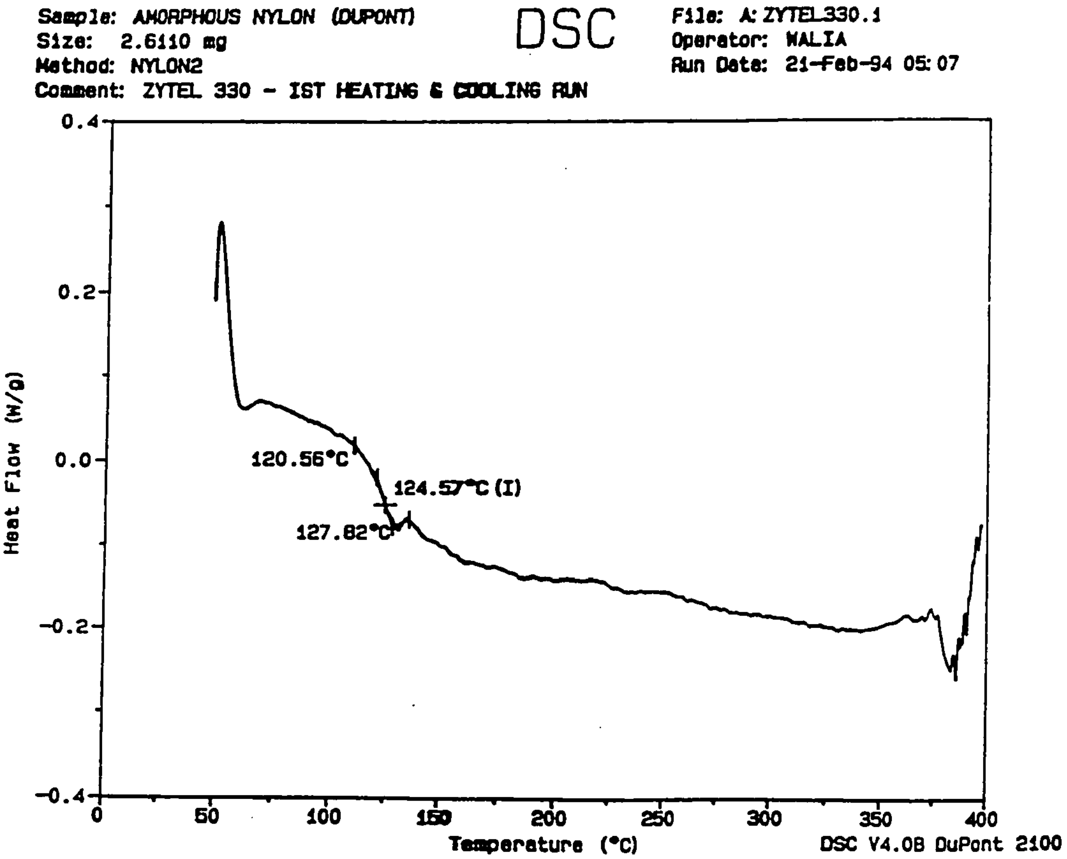


FIGURE A.8: DSC Heating Run for Zytel 330 (Amorphous Nylon, Dupont)

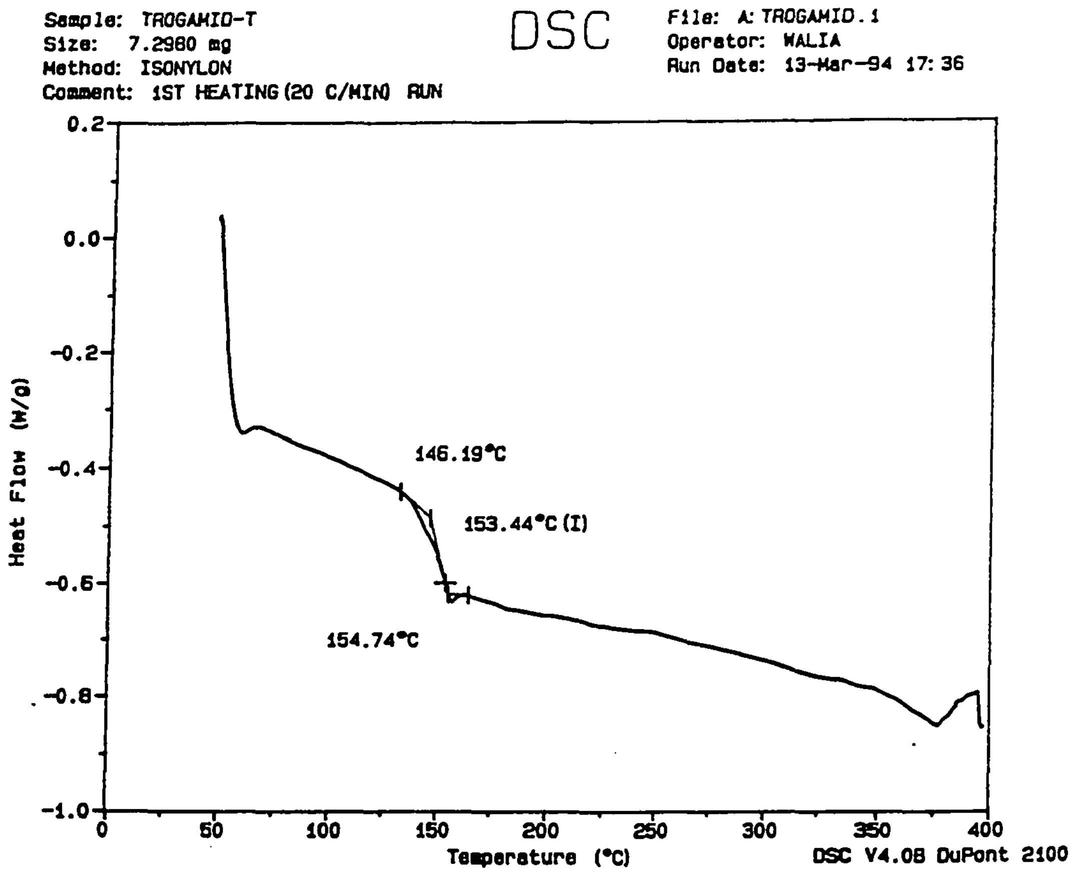


FIGURE A.9: DSC Heating Run for Trogamid-T (Amorphous Nylon, Huls-America)

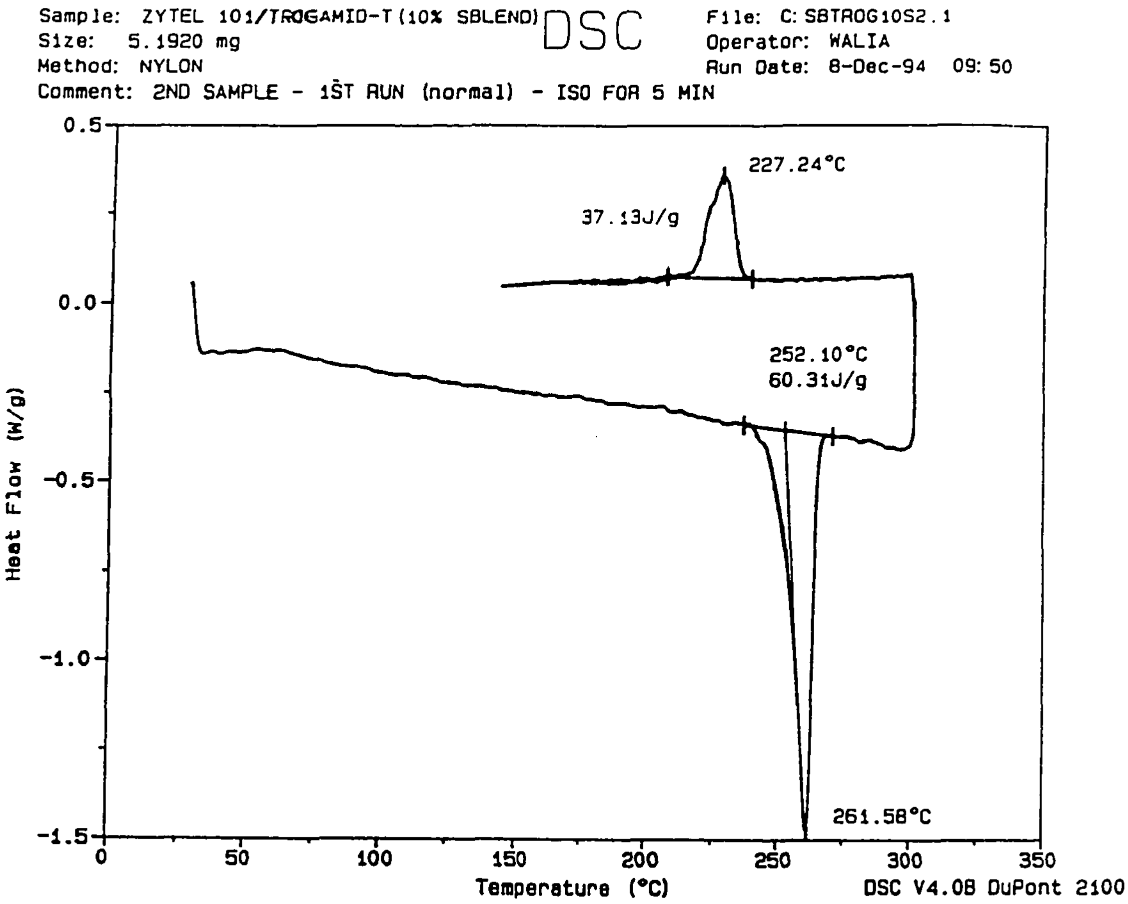


FIGURE A.10: First Heating & Cooling Run for a Zytel 101/Trogamid-T (10% Solution Blend)

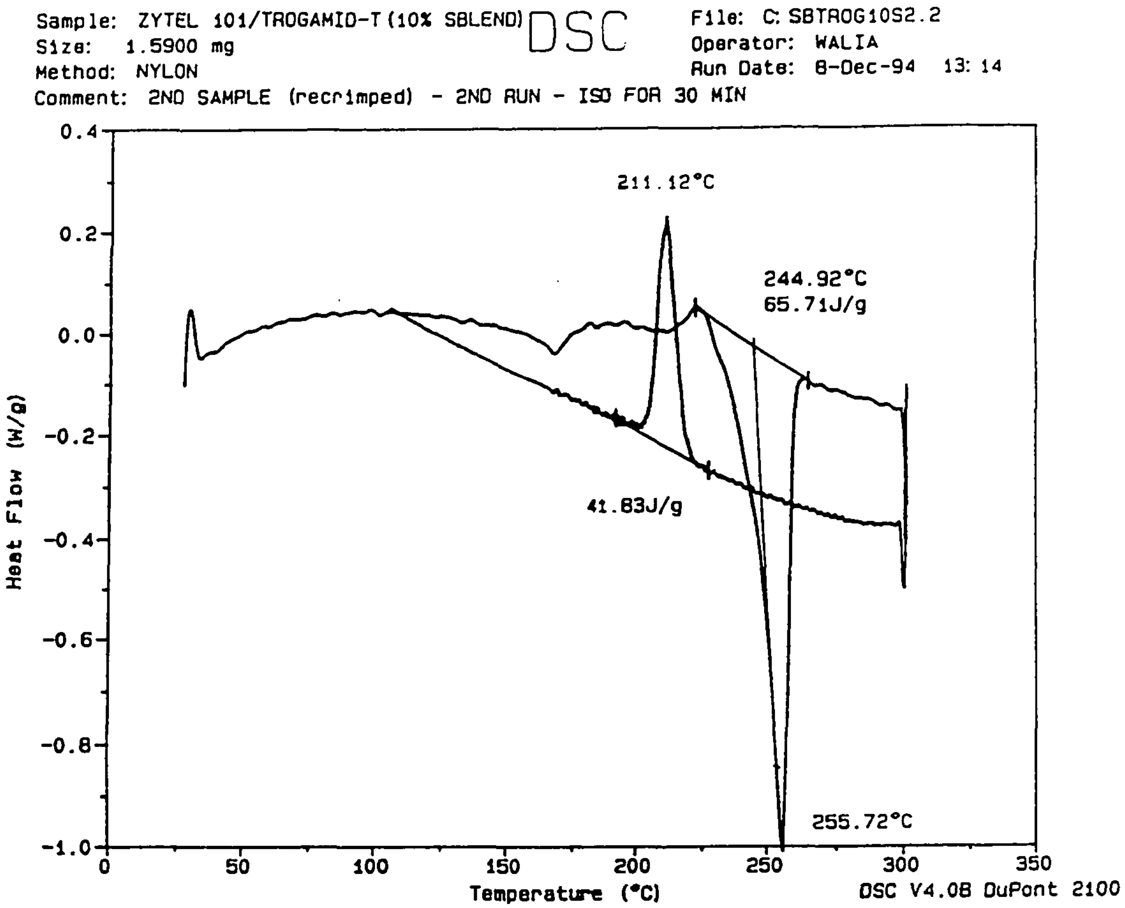


FIGURE A.11: Second Heating & Cooling Run for a Zytel 101/Trogamid-T (10% Solution Blend), Isothermal for 30 mins

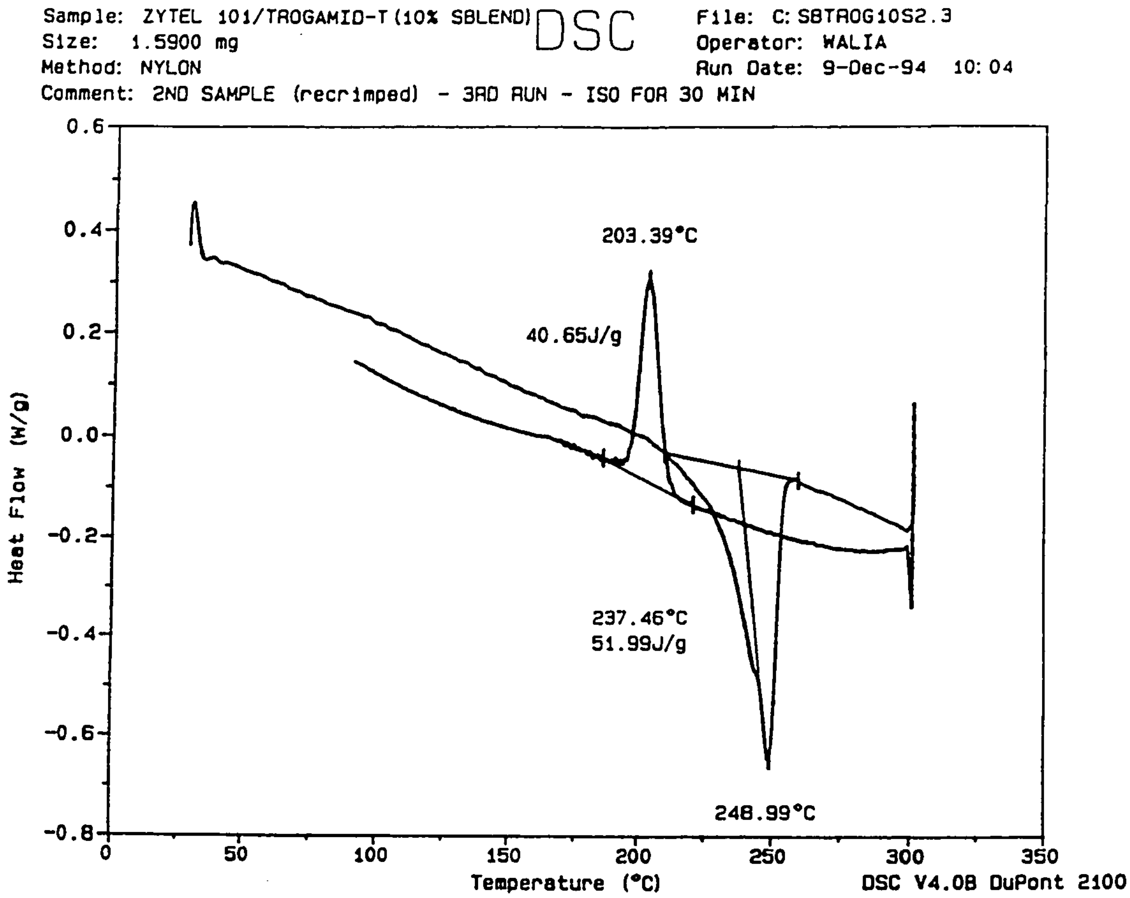


FIGURE A.12: Third Heating & Cooling Run for a Zytel 101/Trogamid-T (10% Solution Blend), Isothermal for 30 mins

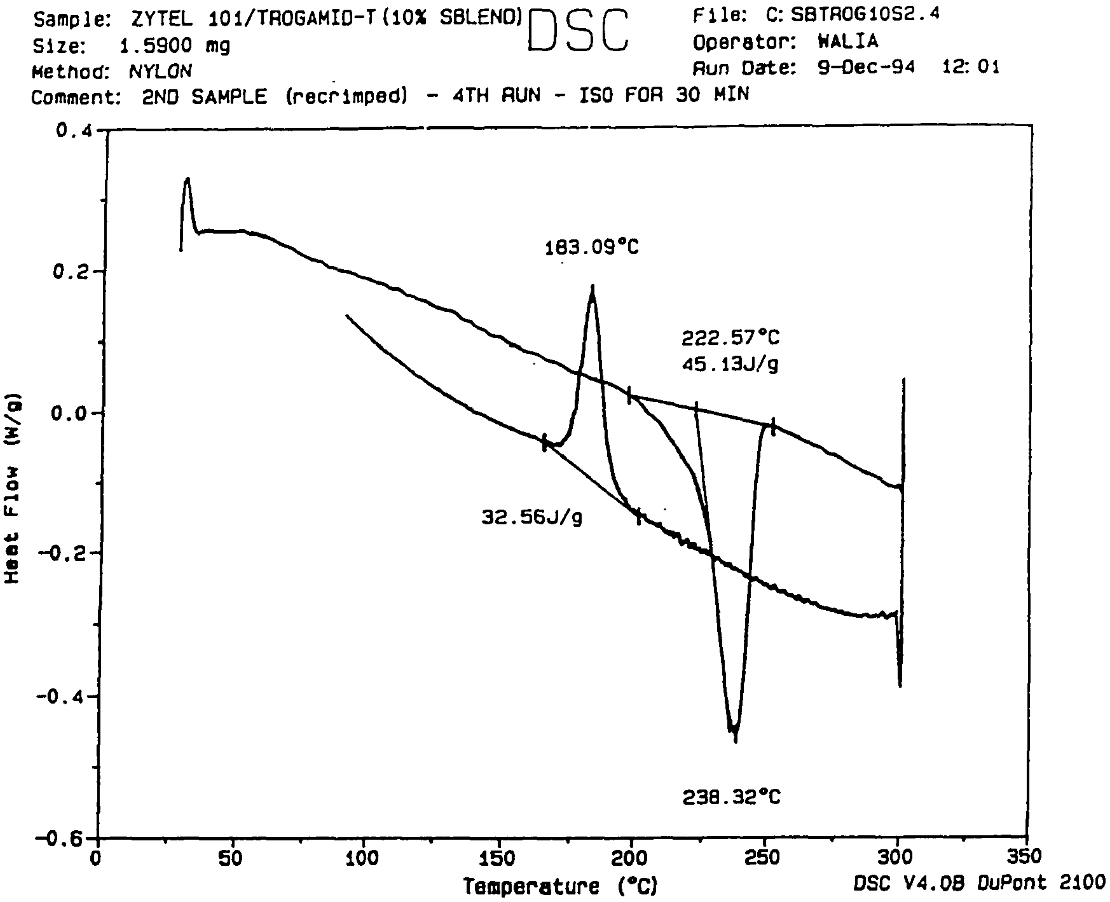
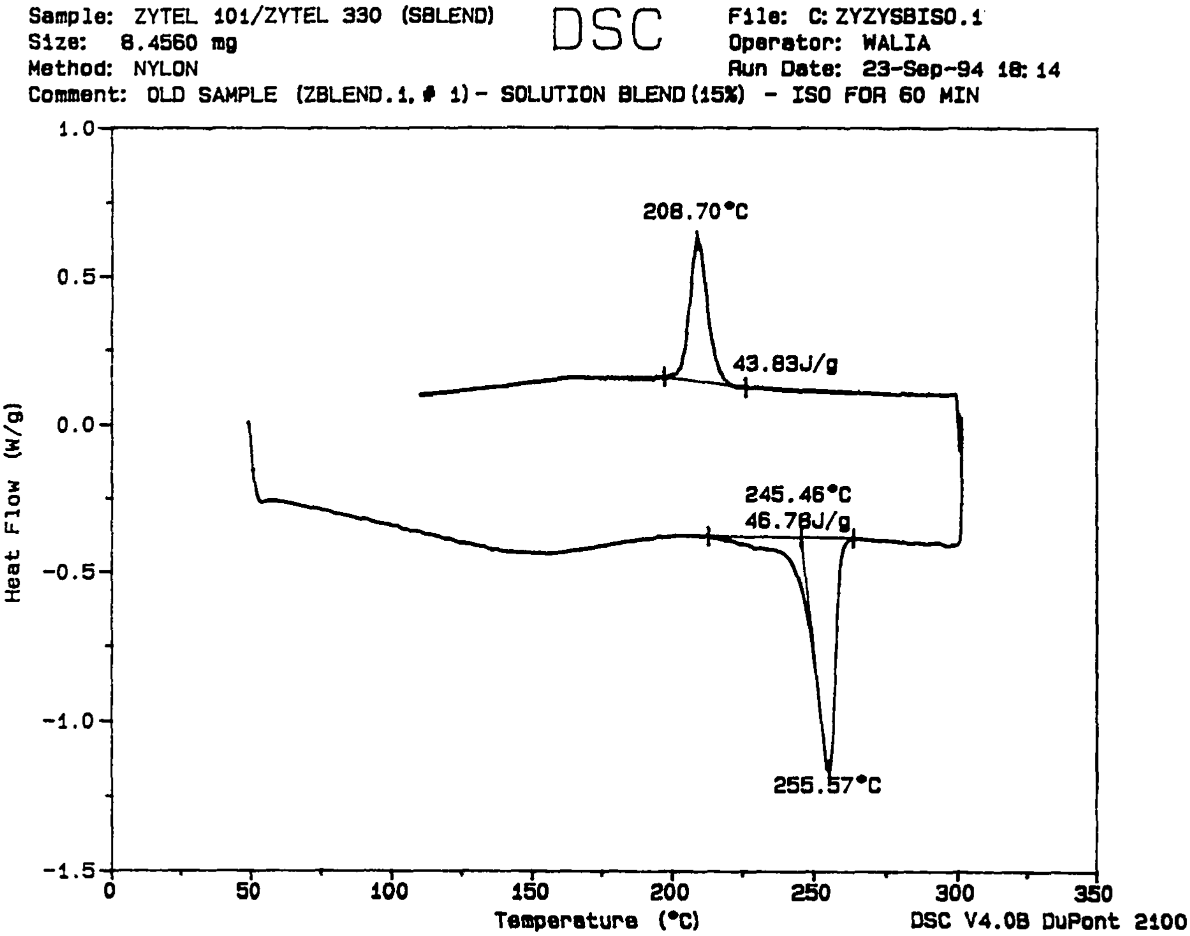


FIGURE A.13: Fourth Heating & Cooling Run for a Zytel 101/Trogamid-T (10% Solution Blend), Isothermal for 30 mins



Sample: ZYTEL 101/ZYTEL 330 (SBLEND)
Size: 8.4560 mg
Method: NYLON
Comment: OLD SAMPLE (ZBLEND.1, # 1) - SOLUTION BLEND(15%) - ISO FOR 60 MIN

File: C: ZYZYSBISO.1
Operator: WALIA
Run Date: 23-Sep-94 18:14

FIGURE A.14: DSC Run for 15% Solution Blend of Nylon 6,6/Zytel 330 After 60 mins of Annealing

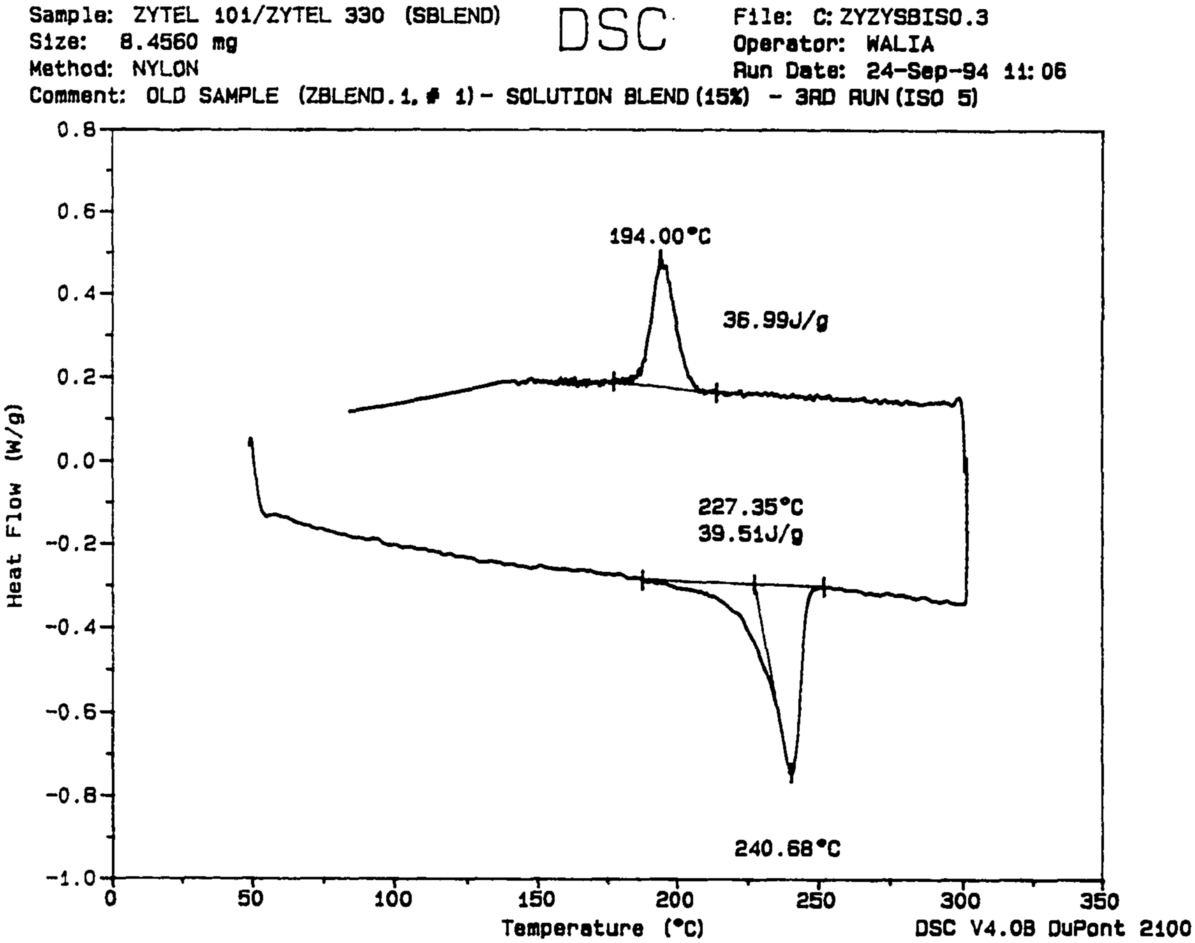


FIGURE A.15: DSC Run for 15% Solution Blend of Nylon 6,6/Zytel 330 After 105 mins of Annealing

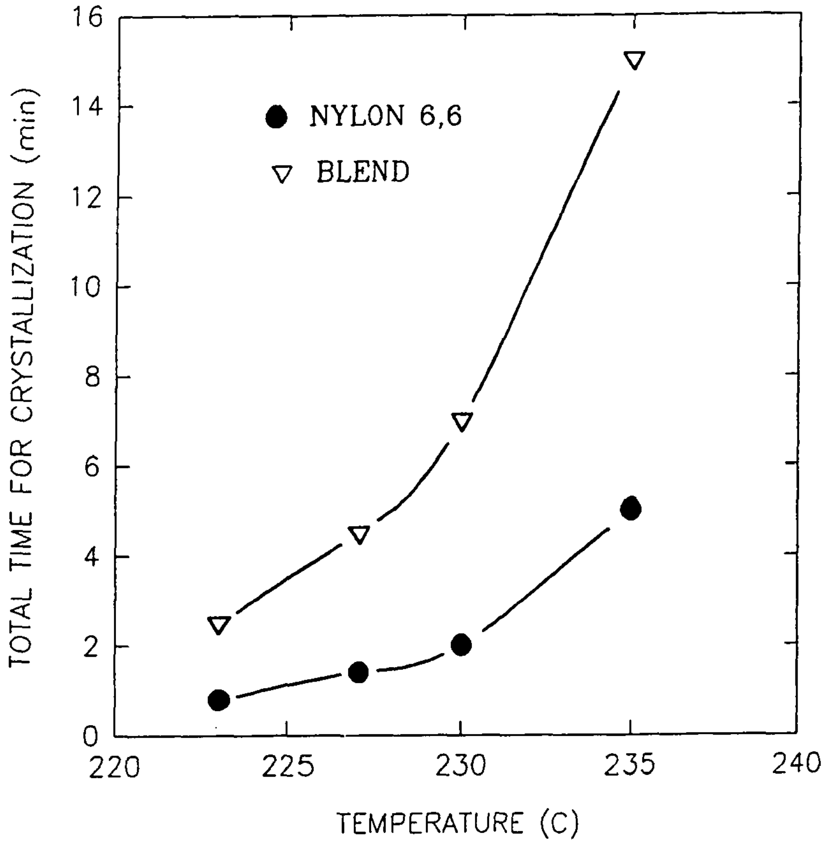


FIGURE A.16: Isothermal Crystallization Times for Pure Zytel 101 and Zytel 101/Zytel 330 (80/20% wt/wt) Blend

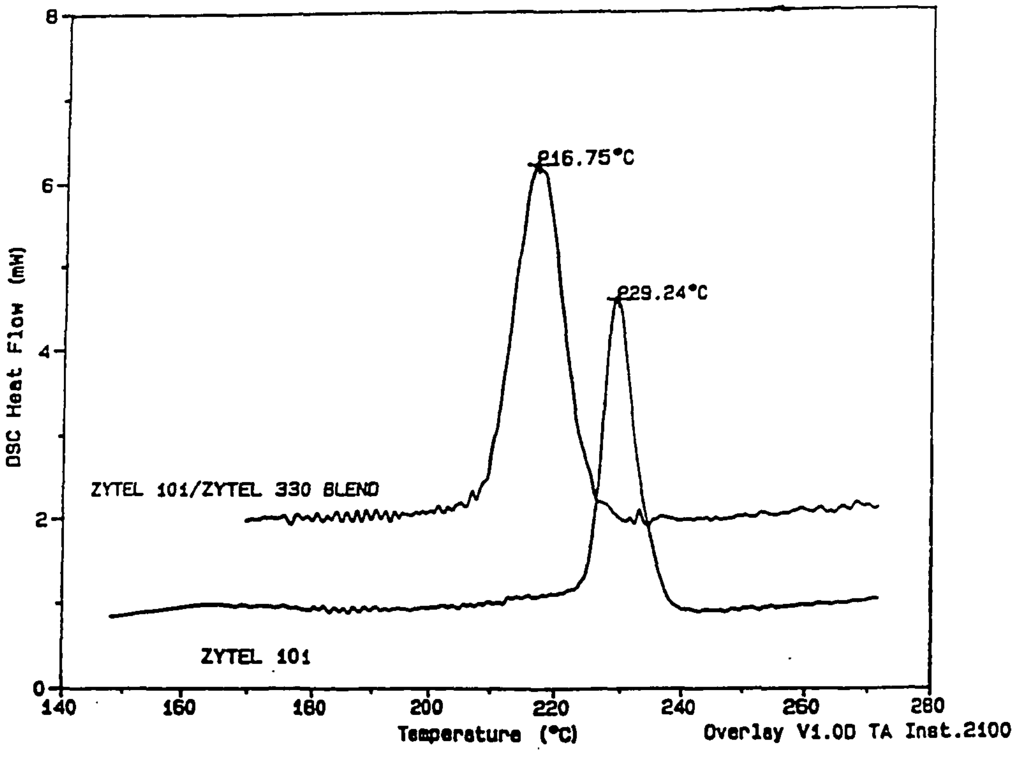


FIGURE A.17: Comparison of Crystallization of Nylon 6,6 and 20% Nylon 6,6/Zytel 330 at 5°C/min Cooling Rate

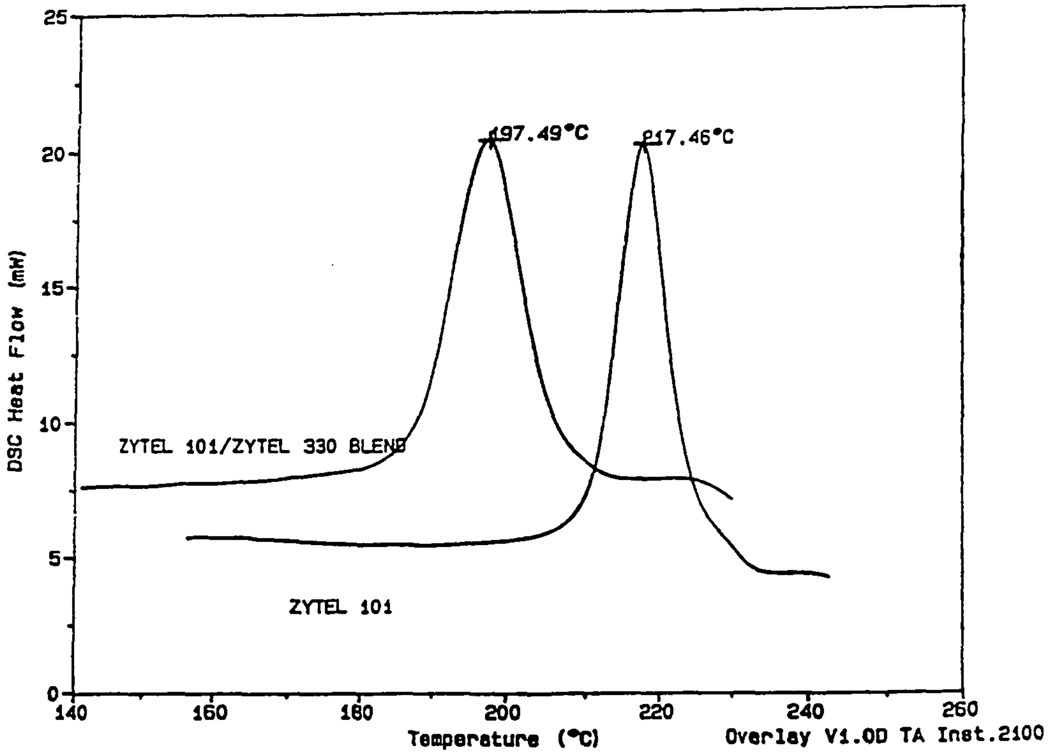


FIGURE A.18 : Comparison of Crystallization of Nylon 6,6 and 20% Nylon 6,6/Zytel 330 at 20°C/min Cooling Rate

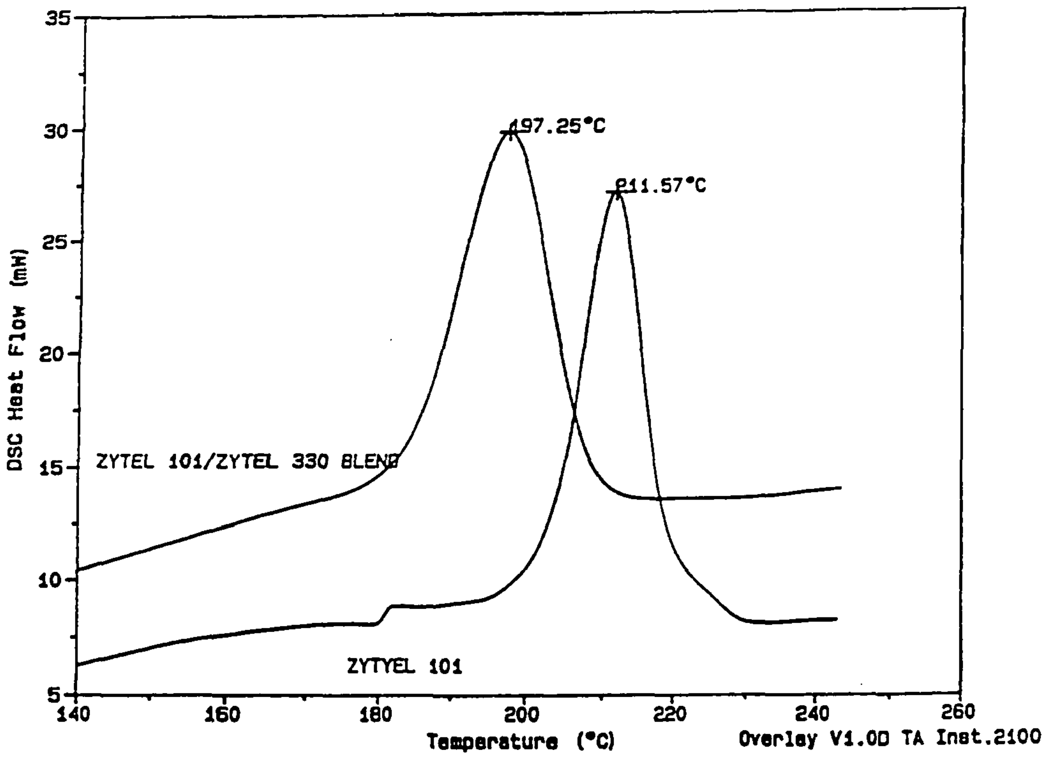
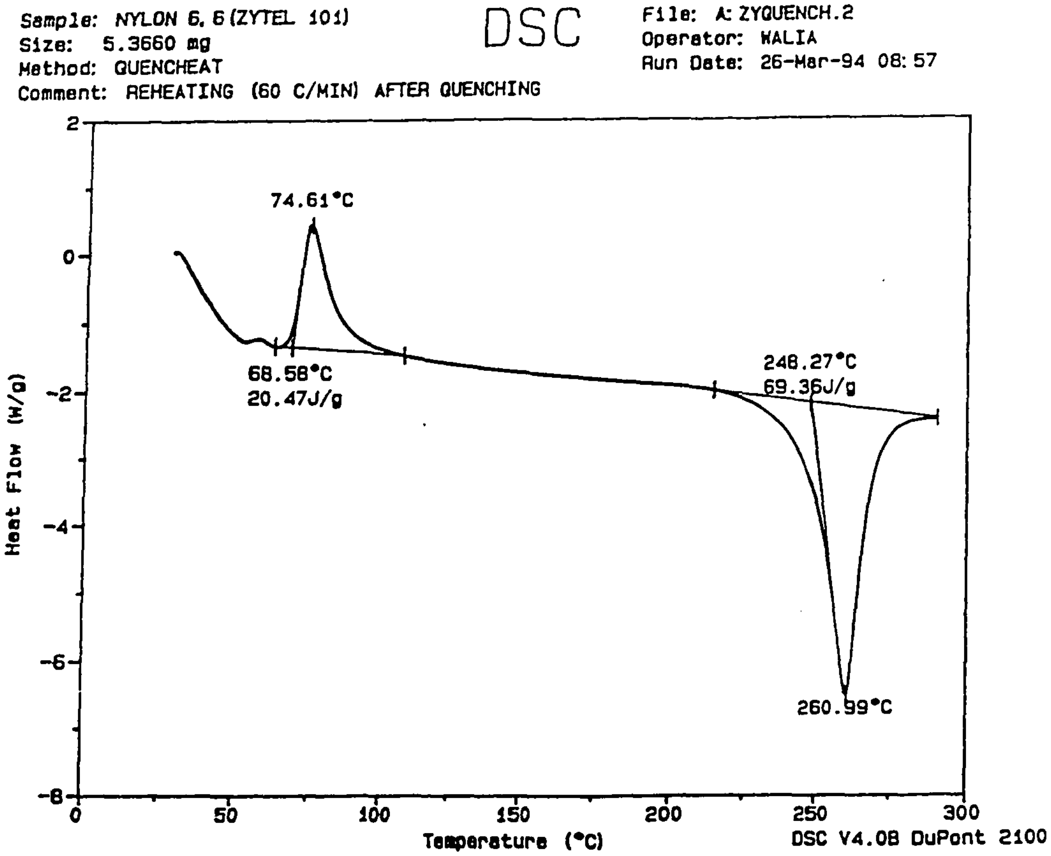


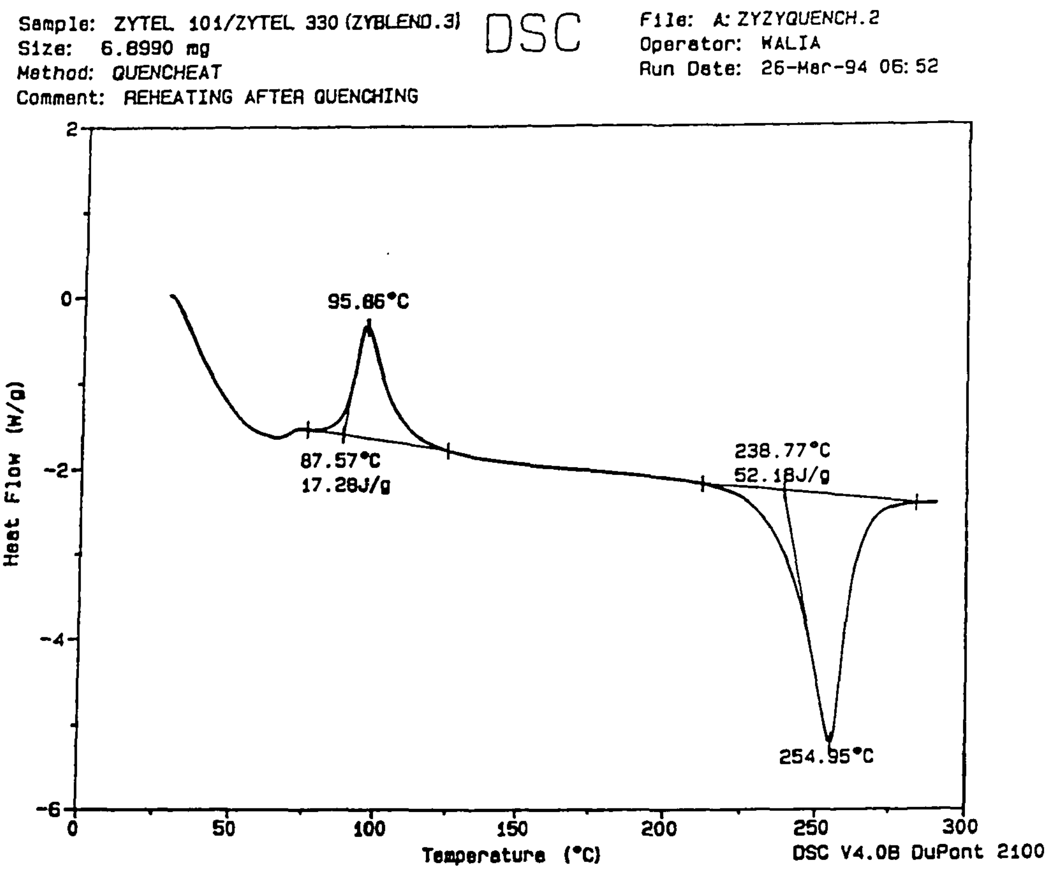
FIGURE A.19: Comparison of Crystallization of Nylon 6,6 and 20% Nylon 6,6/Zytel 330 at 40°C/min Cooling Rate



CRYSTALLINITY OF QUENCHED POLYMER = 26 %

FINAL CRYSTALLINITY = 36.9 %

FIGURE A.20: Heating (60°C/min) Run for Quenched Nylon 6,6



CRYSTALLINITY OF QUENCHED BLEND = 23.2 %

FINAL CRYSTALLINITY = 34.7 %

FIGURE A.21: Heating (60°C/min) Run for Quenched Zytel 101/Zytel 330 Blend Sample

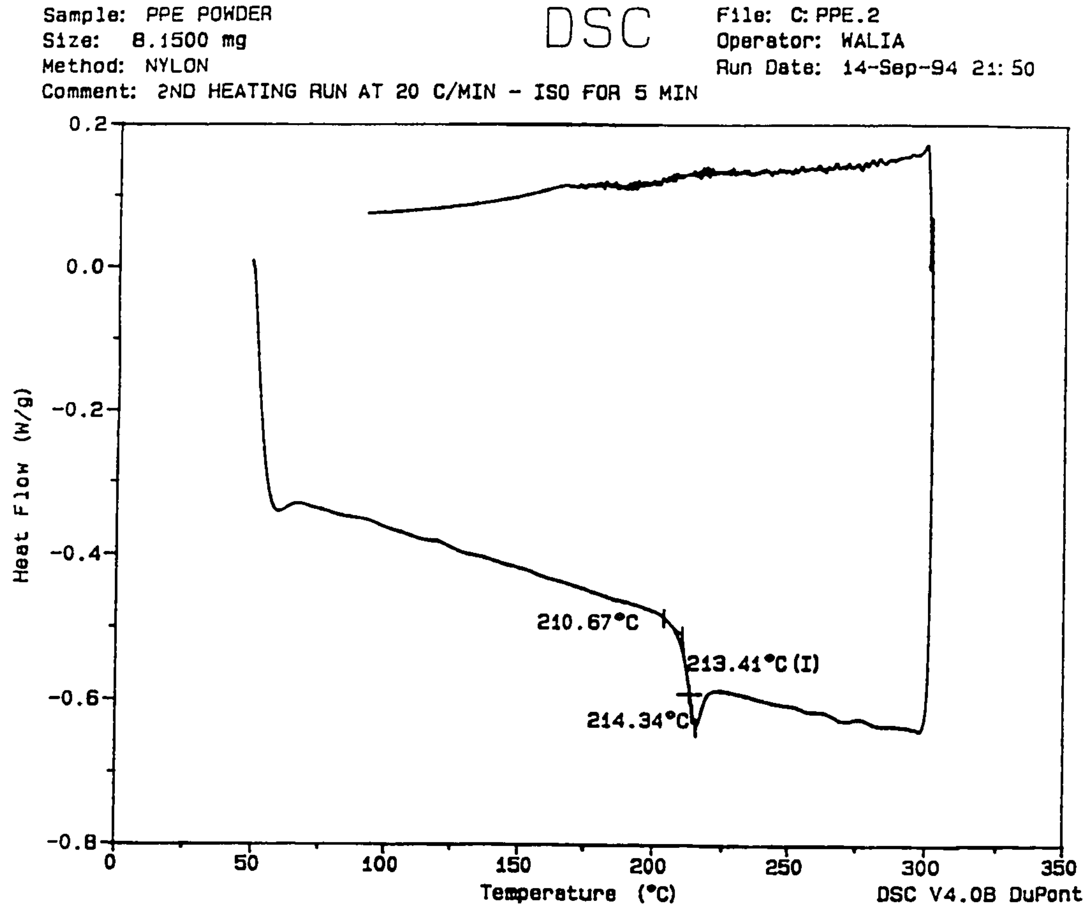
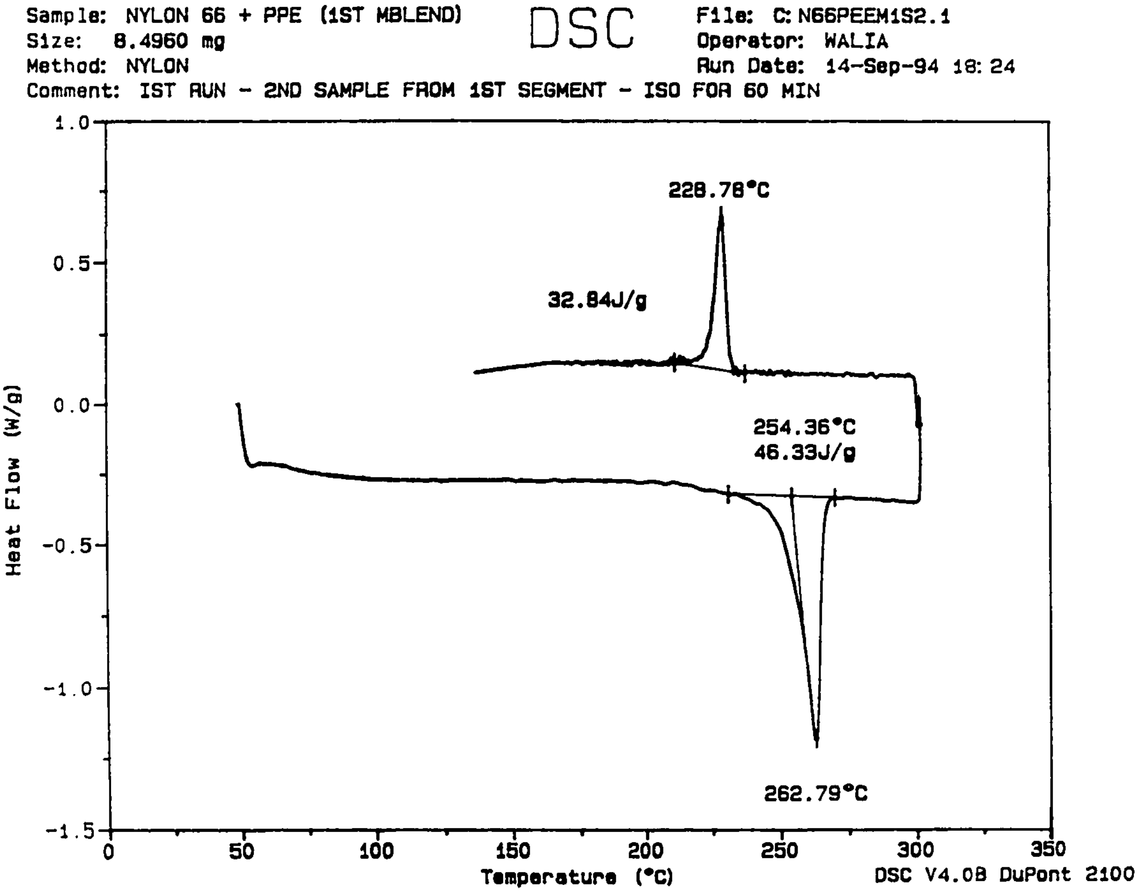


FIGURE A.22: DSC Run for Pure Polyphenylene Ether (PPE) Powder



Sample: NYLON 66 + PPE (1ST MBLEND)
Size: 8.4960 mg
Method: NYLON
Comment: IST RUN - 2ND SAMPLE FROM 1ST SEGMENT - ISO FOR 60 MIN

File: C:N66PEEM1S2.1
Operator: WALIA
Run Date: 14-Sep-94 18:24

FIGURE A.23: DSC First Run for a Nylon 6,6/Polyphenylene Ether (75/25% wt/wt) Blend, Isothermal for 60 mins

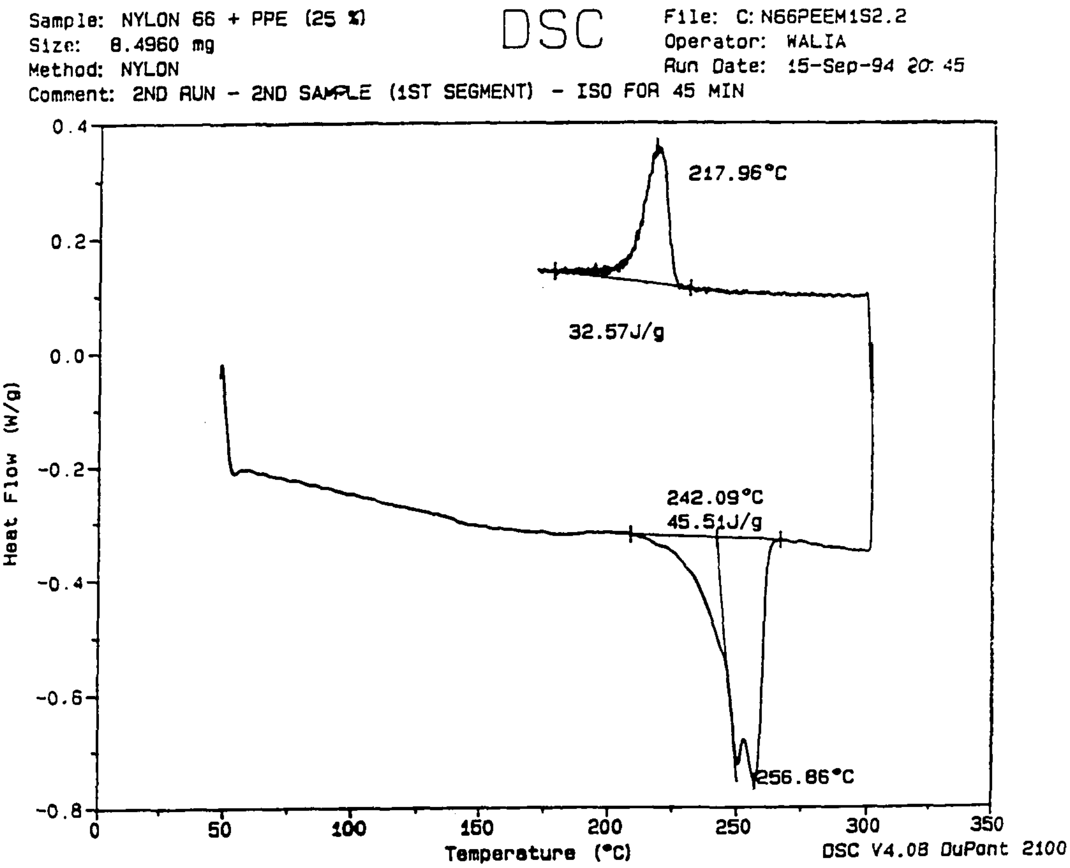


FIGURE A.24: DSC Second Run for a Nylon 6,6/Polyphenylene Ether (75/25% wt/wt) Blend, Isothermal for 45 mins

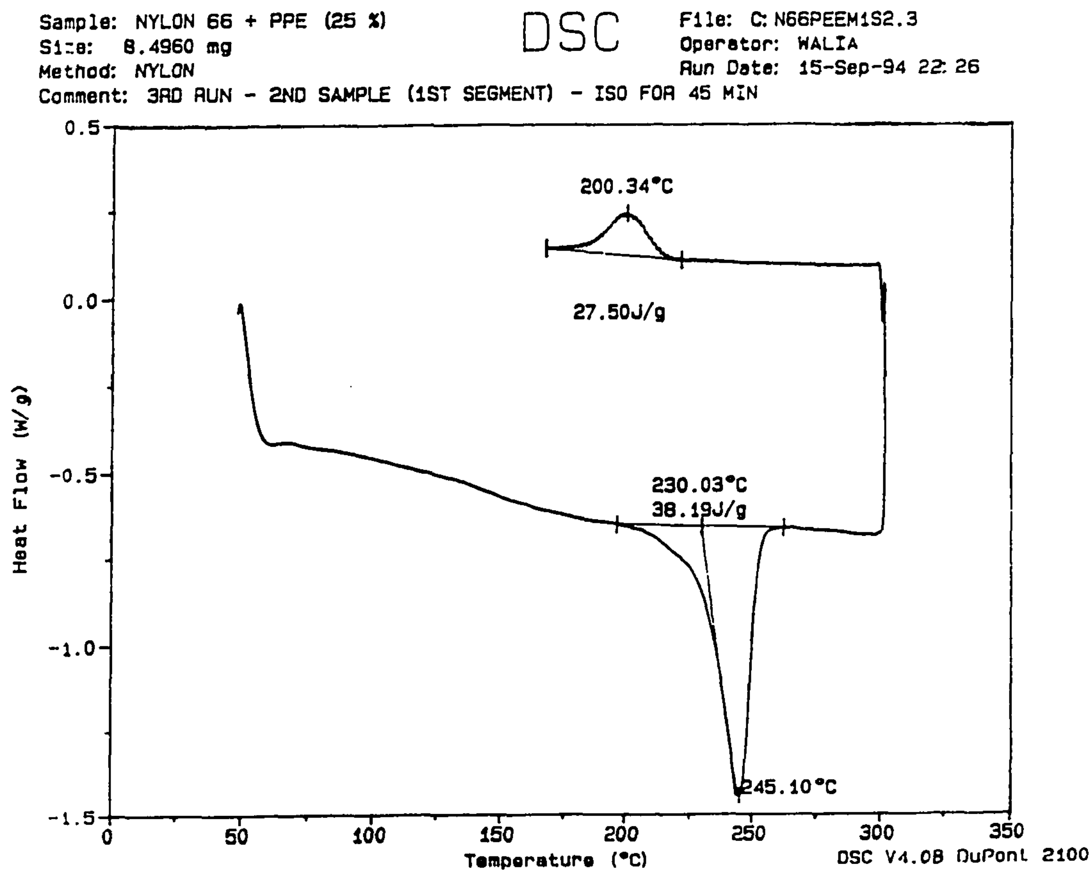


FIGURE A.25: DSC Third Run for a Nylon 6,6/Polyphenylene Ether (75/25% wt/wt) Blend, Isothermal for 45 mins

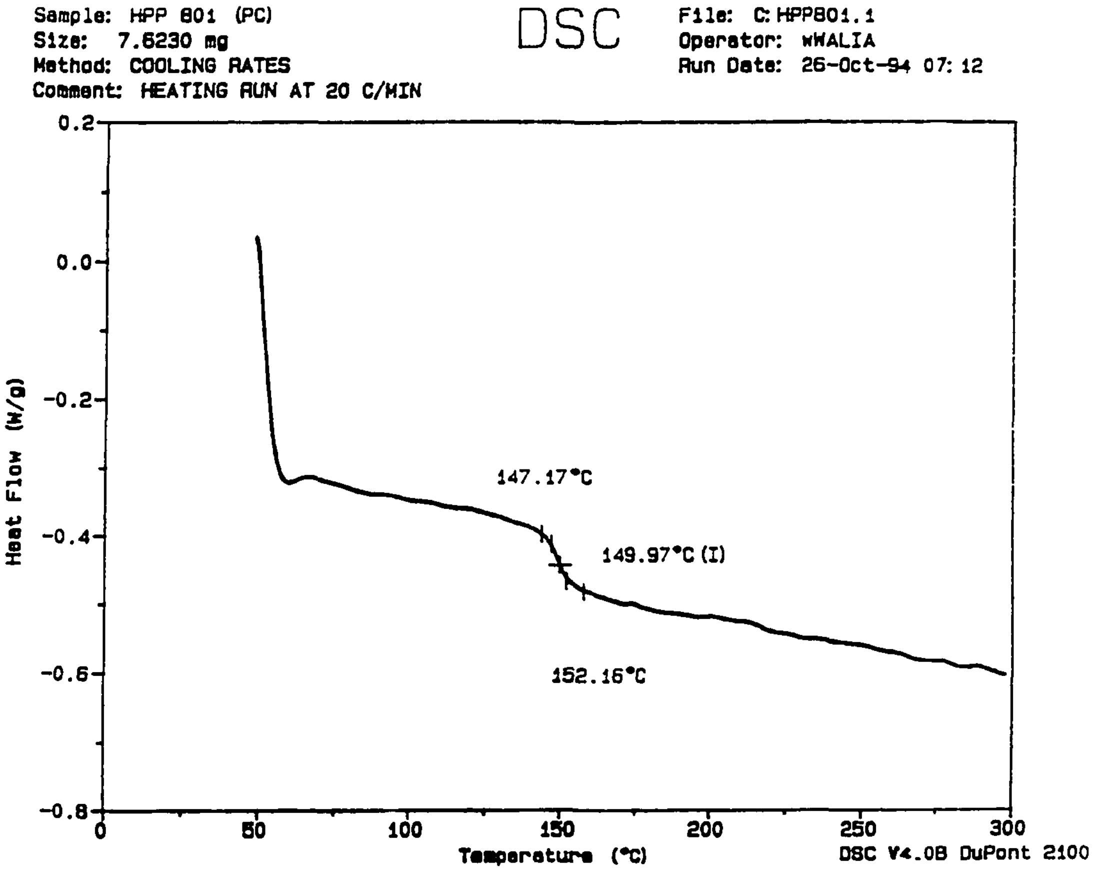
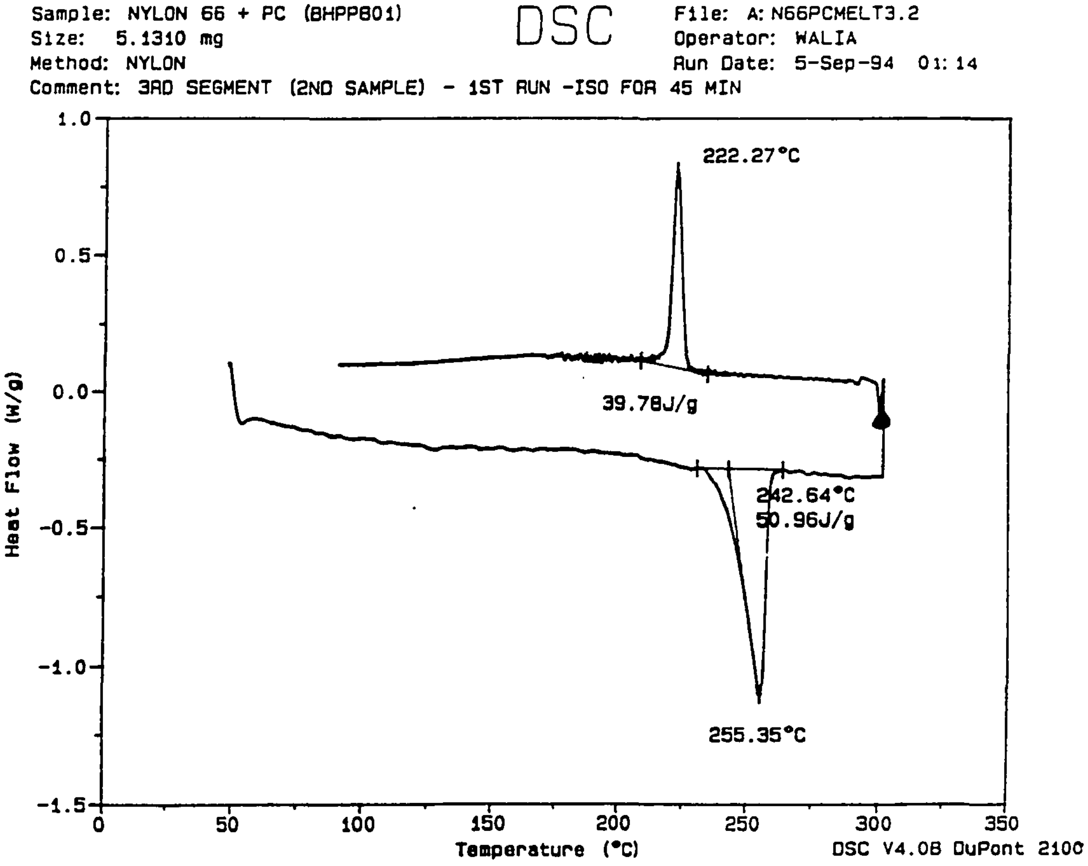


FIGURE A.26: DSC Run for Polycarbonate (HPP 801, GE Plastics)



Sample: NYLON 66 + PC (BHPP801)
Size: 5.1310 mg
Method: NYLON
Comment: 3RD SEGMENT (2ND SAMPLE) - 1ST RUN -ISO FOR 45 MIN
File: A: N66PCMELT3.2
Operator: WALIA
Run Date: 5-Sep-94 01: 14

FIGURE A.27: First Run for a Nylon 6,6/Polycarbonate (HPP 801) (75/25% wt/wt) Melt Blend, Isothermal for 45 mins

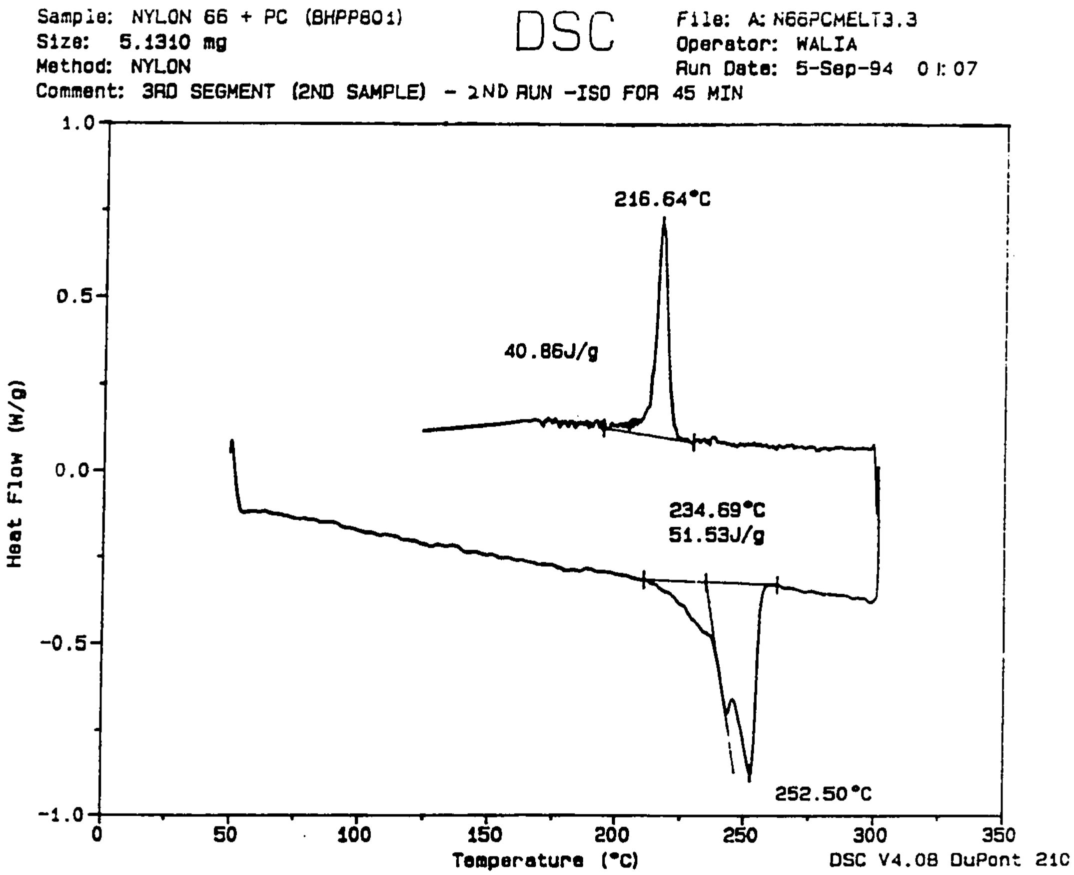


FIGURE A.28: Second Run for a Nylon 6,6/Polycarbonate (HPP 801) (75/25% wt/wt) Melt Blend, Isothermal for 45 mins

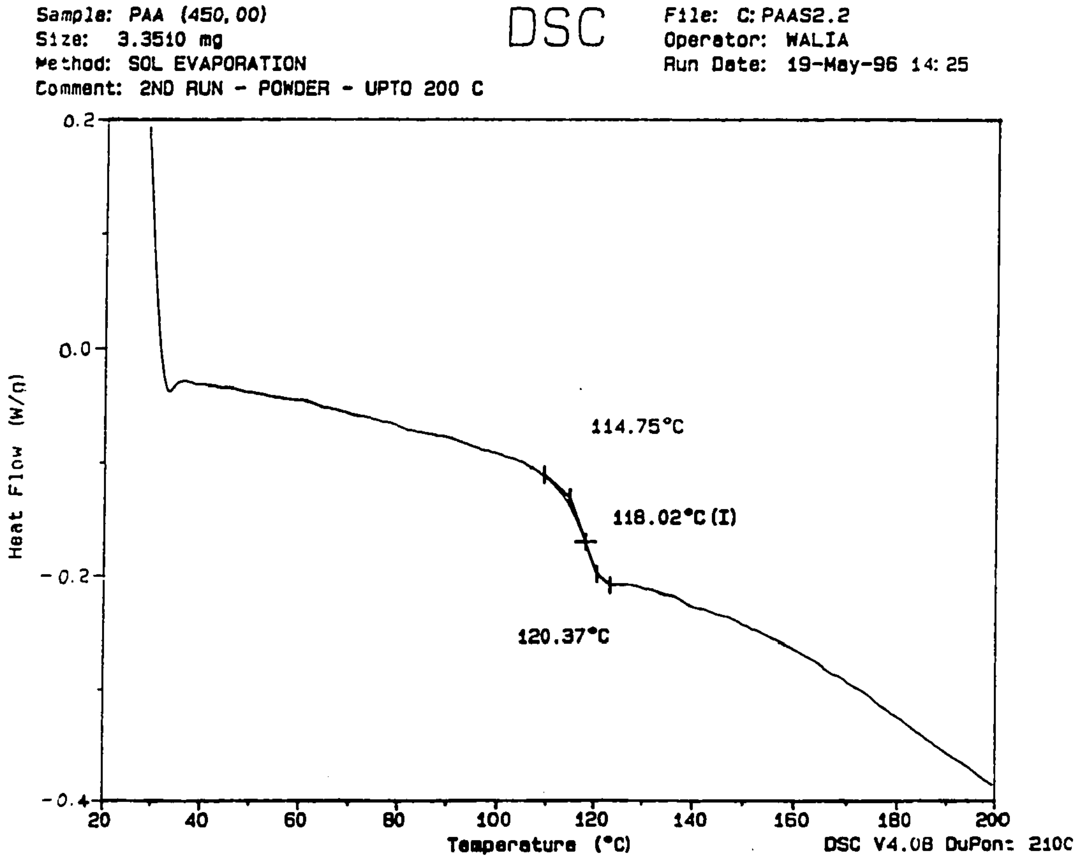


FIGURE A.29: DSC Heating Run for Polyacrylic Acid (PAA)

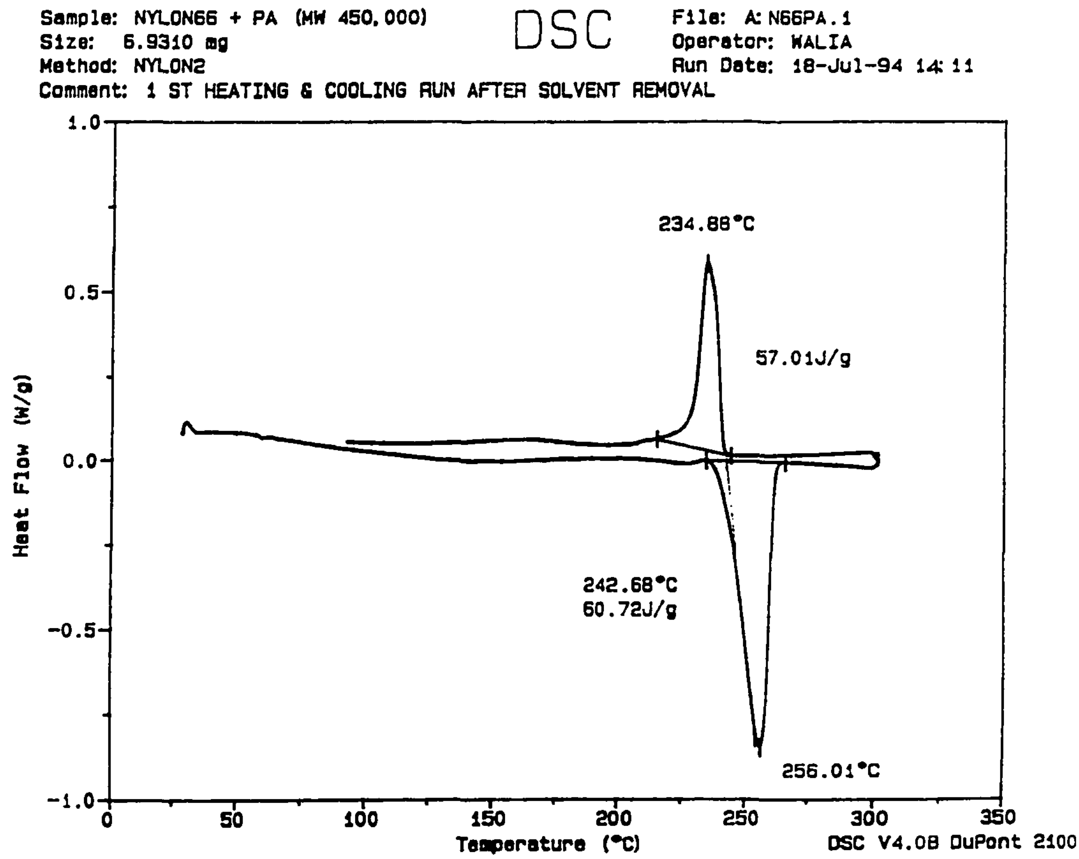


FIGURE A.30: First Run for a Nylon 6,6/Polyacrylic Acid (PAA) (15% Solution Blend)

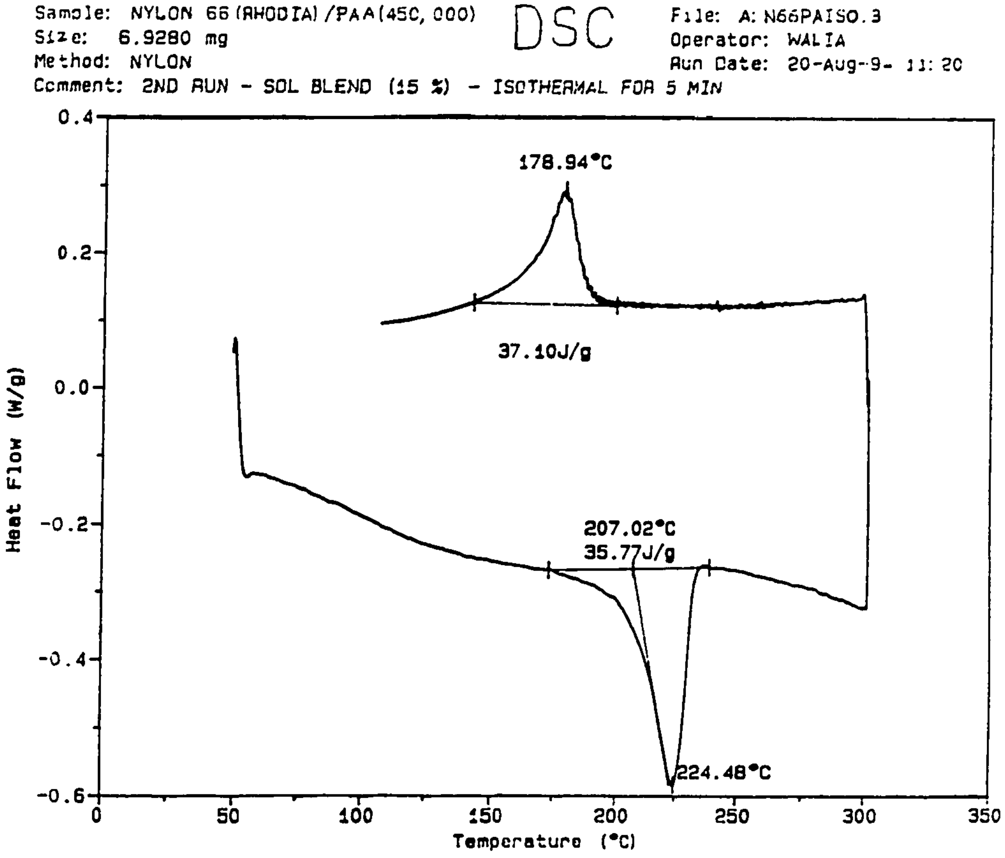


FIGURE A.31: Second Run for a Nylon 6,6/Polyacrylic Acid (PAA) (15% Solution Blend) After Having Been Annealed for 60 mins

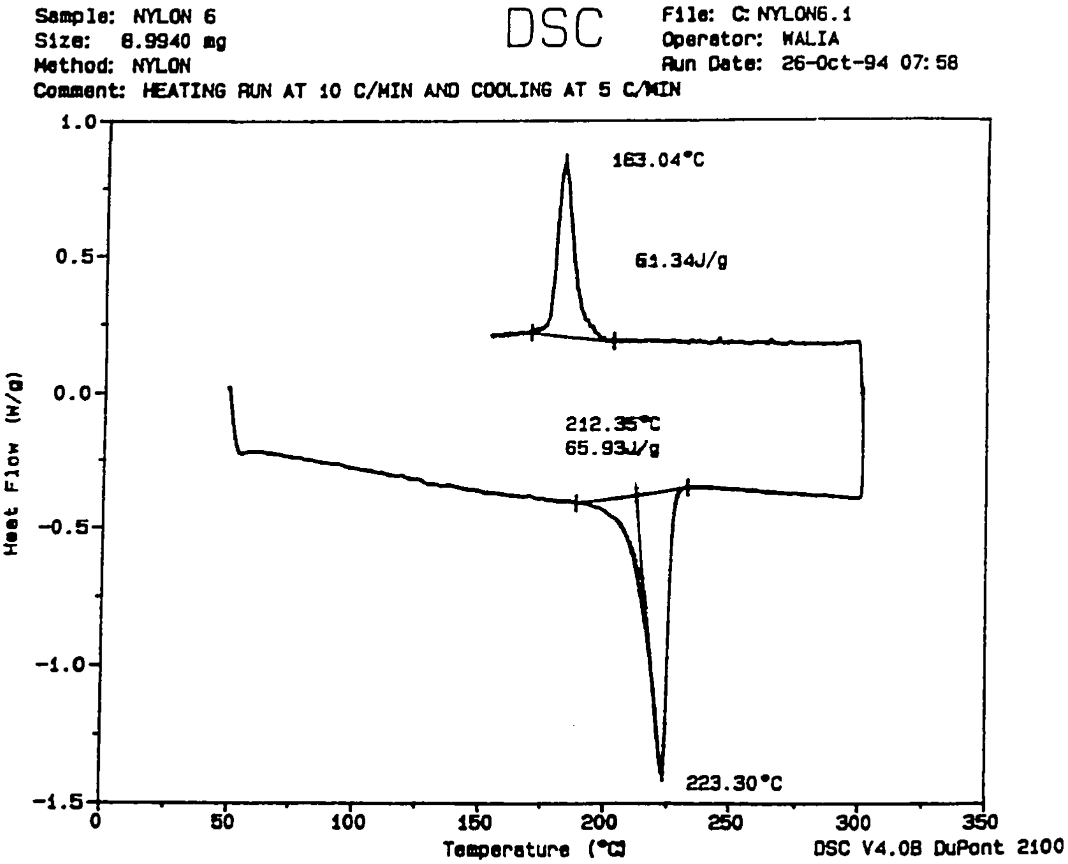


FIGURE A.32: DSC Run for Pure Nylon 6

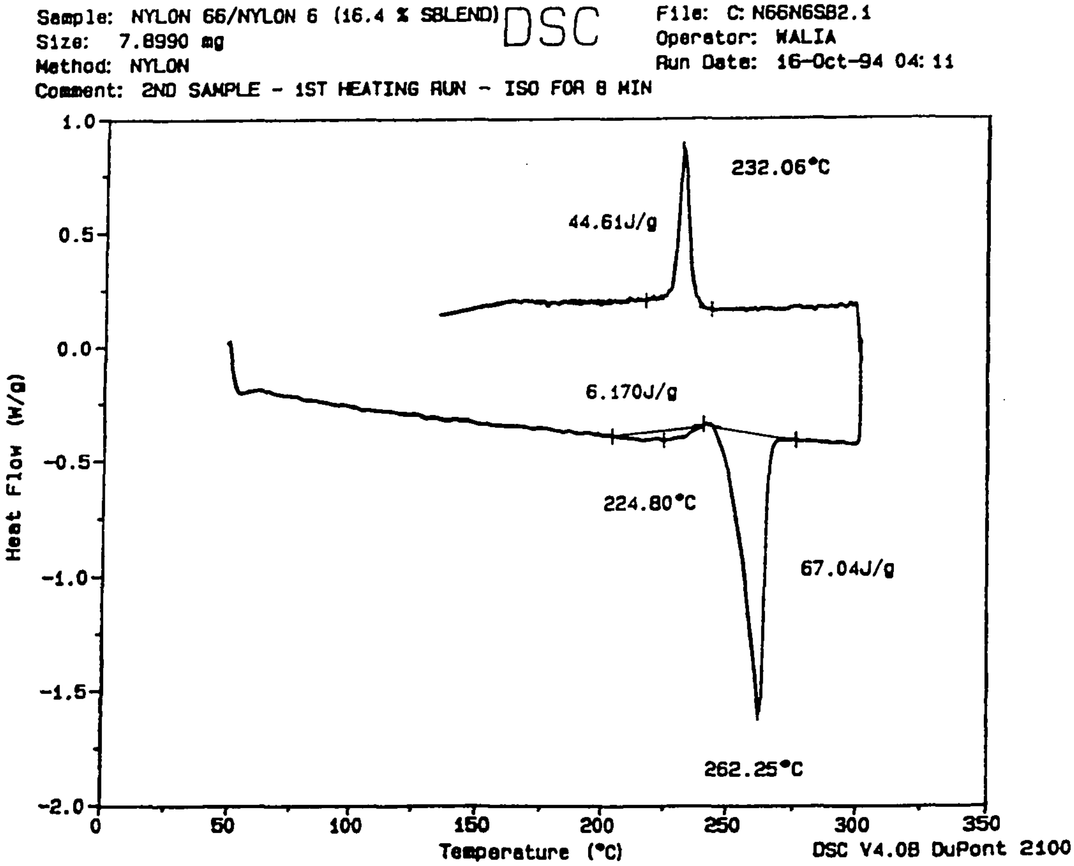


FIGURE A.33: First Run for a Nylon 6,6/Nylon 6 (16.4% Solution Blend)

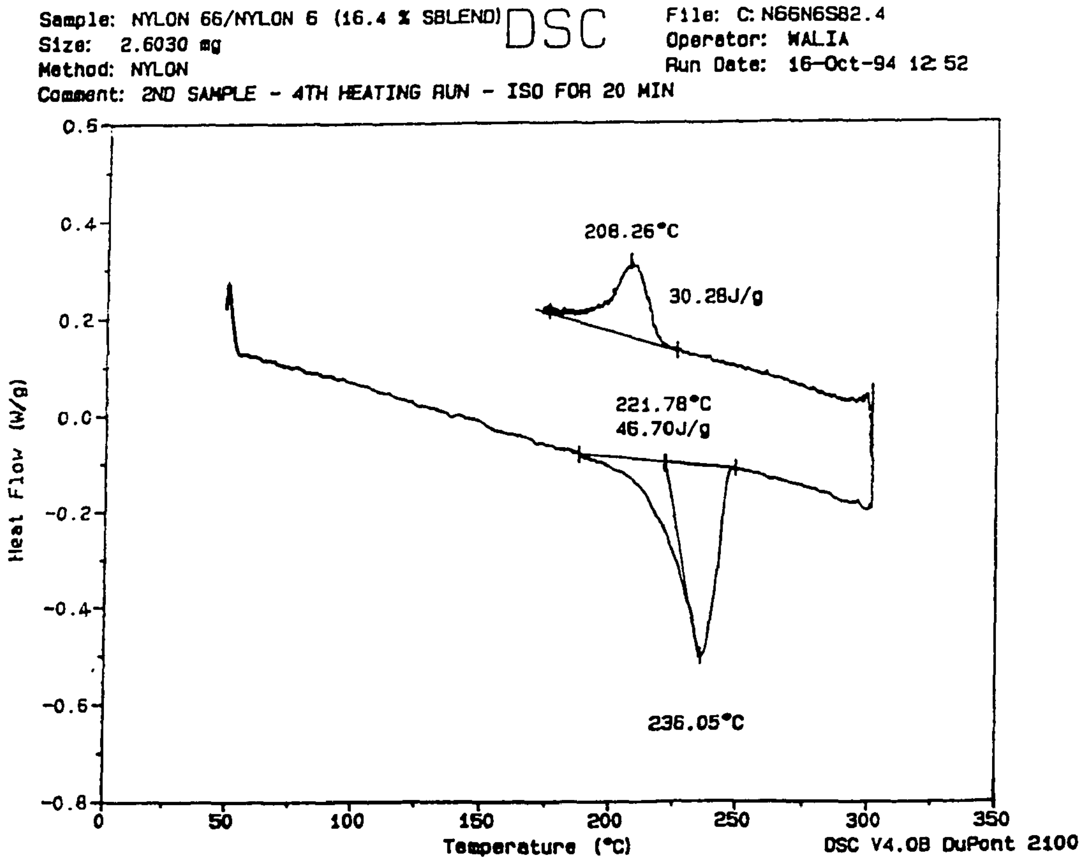


FIGURE A.34: DSC Run for a Nylon 6,6/Nylon 6 (16.4% Solution Blend) After Annealing at 300°C for 70 mins

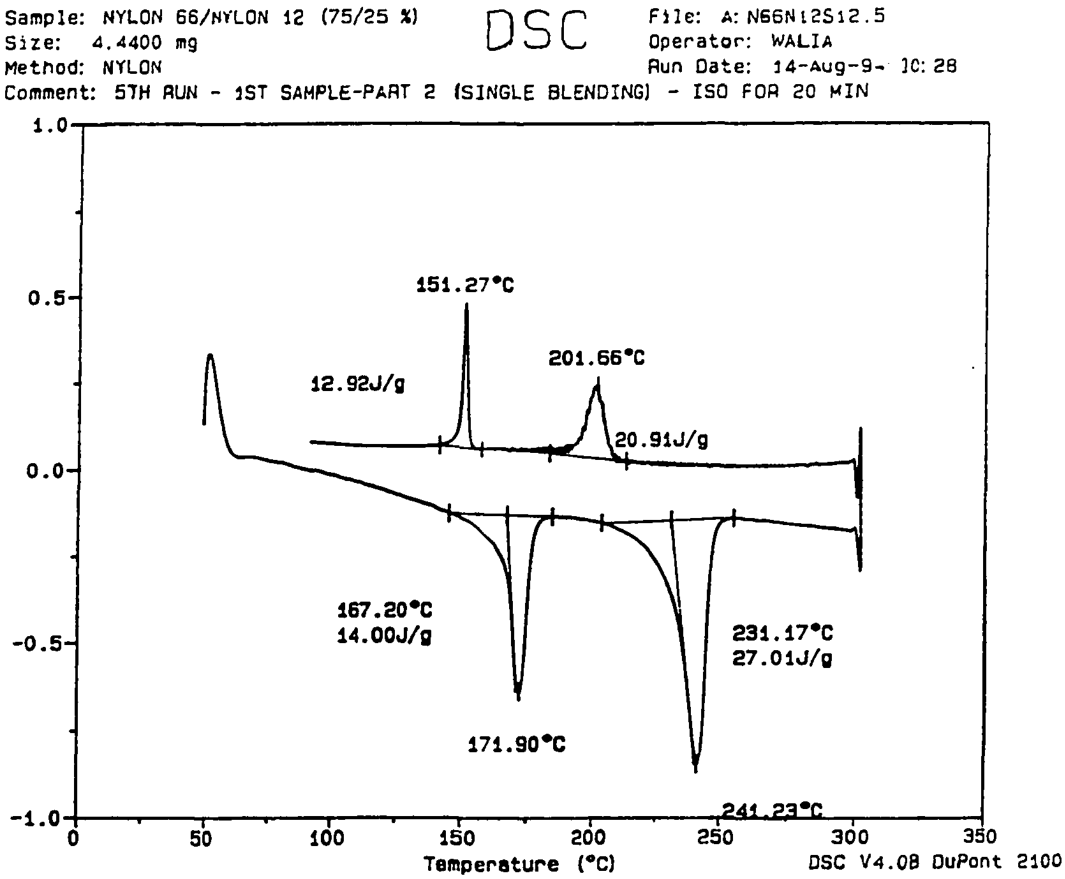

Sample: NYLON 66/NYLON 12 (75/25 %)
Size: 4.4400 mg
Method: NYLON
Comment: 5TH RUN - 1ST SAMPLE-PART 2 (SINGLE BLENDING) - ISO FOR 20 MIN
File: A:N66N12S12.5
Operator: WALIA
Run Date: 14-Aug-9- 10: 28

FIGURE A.35: DSC Run for a Nylon 6,6/Nylon 12 (25% Melt Blend) After Annealing at 300°C for 60 mins

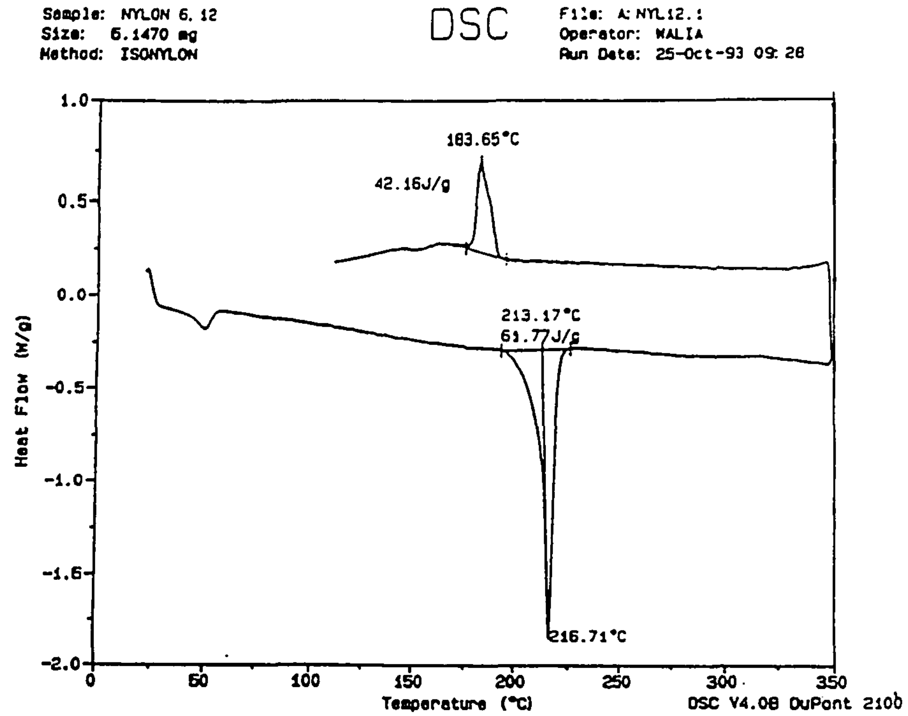
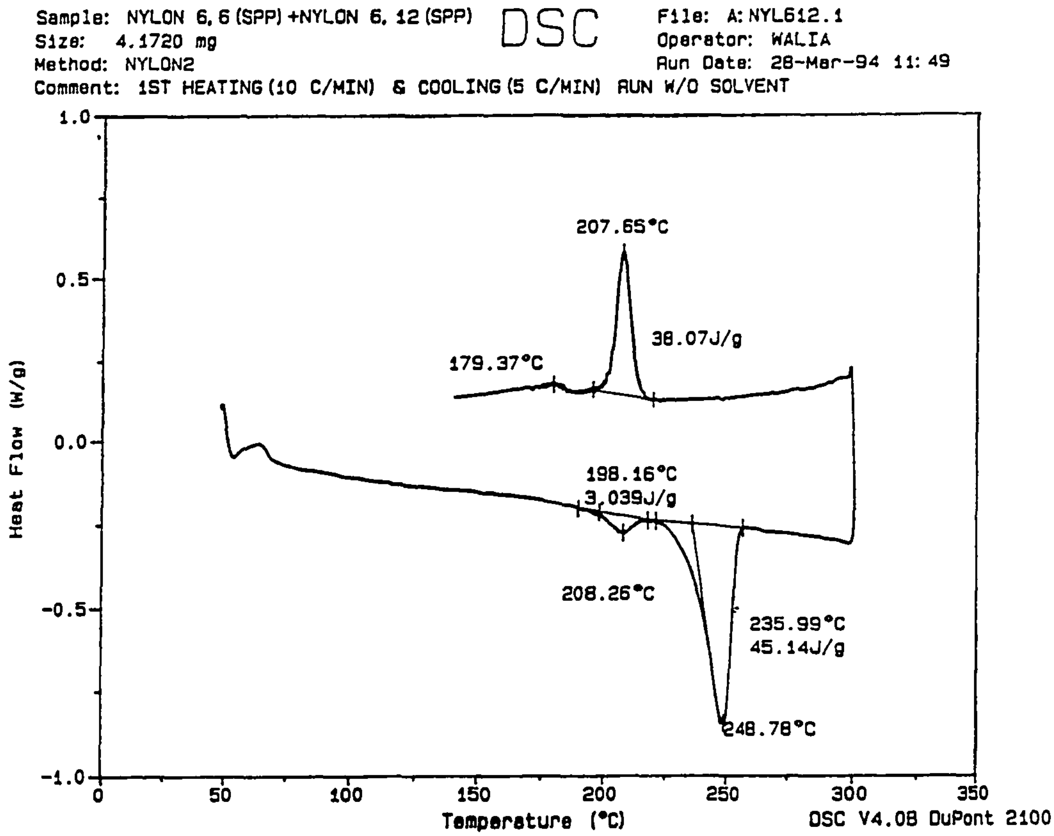


FIGURE A.36: DSC Run for Pure Nylon 6,12



Sample: NYLON 6,6 (SPP) +NYLON 6,12 (SPP)
Size: 4.1720 mg
Method: NYLON2
Comment: 1ST HEATING (10 C/MIN) & COOLING (5 C/MIN) RUN W/O SOLVENT
File: A:NYL612.1
Operator: WALIA
Run Date: 28-Mar-94 11:49

FIGURE A.37: First Heating & Cooling Run for a Nylon 6,6/Nylon 6,12 (25% Solution Blend)

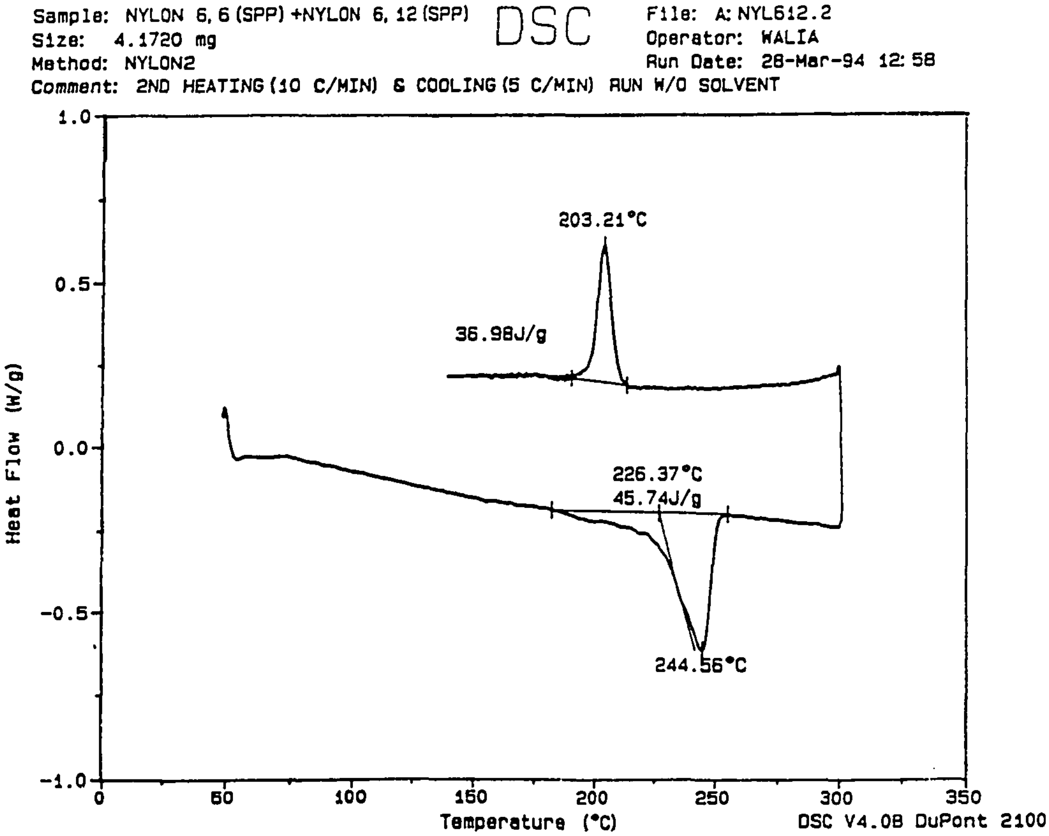


FIGURE A.38: Second Heating & Cooling Run for a Nylon 6,6/Nylon 6,12 (25% Solution Blend)

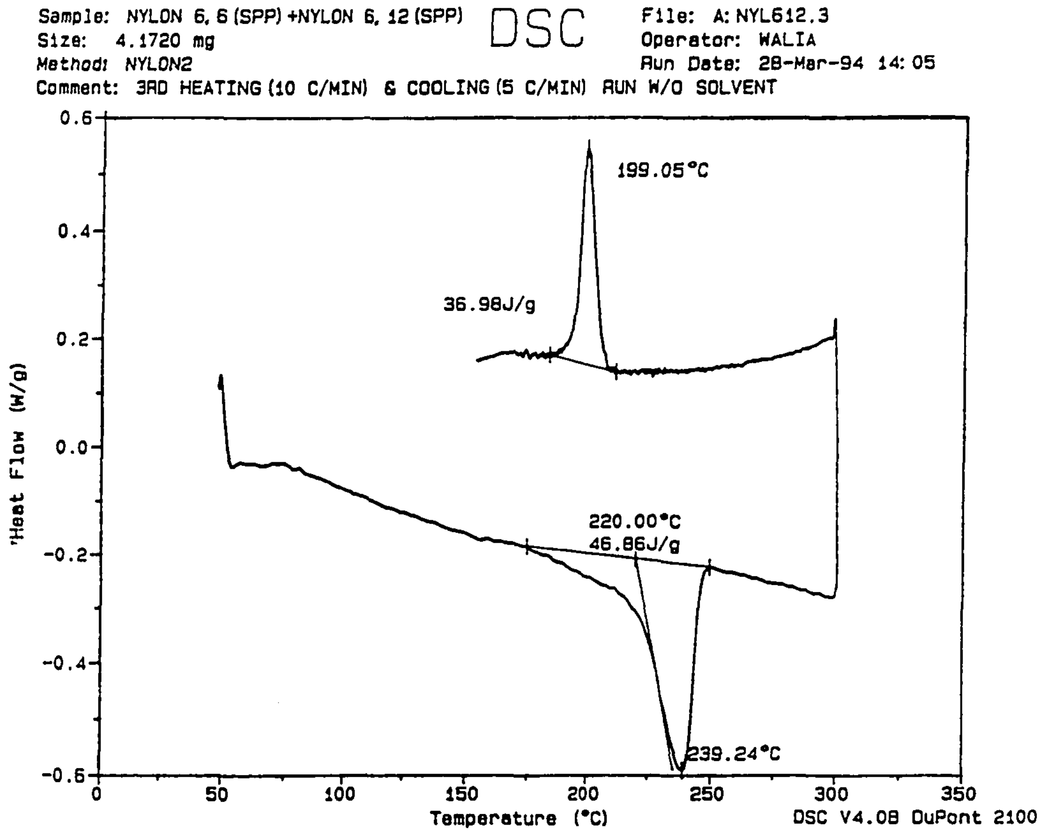
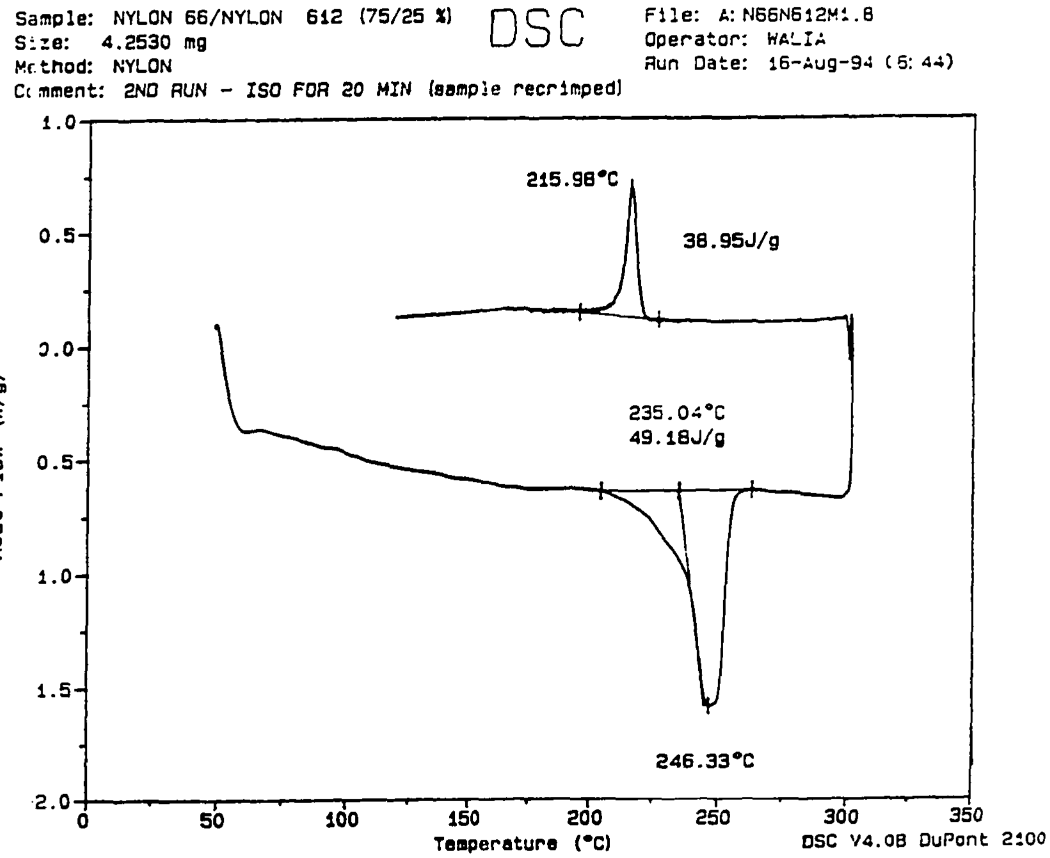


FIGURE A.39: Third Heating & Cooling Run for a Nylon 6,6/Nylon 6,12 (25% Solution Blend)



Sample: NYLON 66/NYLON 612 (75/25 %)
Size: 4.2530 mg
Method: NYLON
Comment: 2ND RUN - ISO FOR 20 MIN (sample recrimped)
File: A:N66N612M1.8
Operator: WALIA
Run Date: 16-Aug-94 (5:44)

FIGURE A.40: DSC Run for a Nylon 6,6/Nylon 6,12 (25% Melt Blend) After Annealing at 300°C for 80 mins

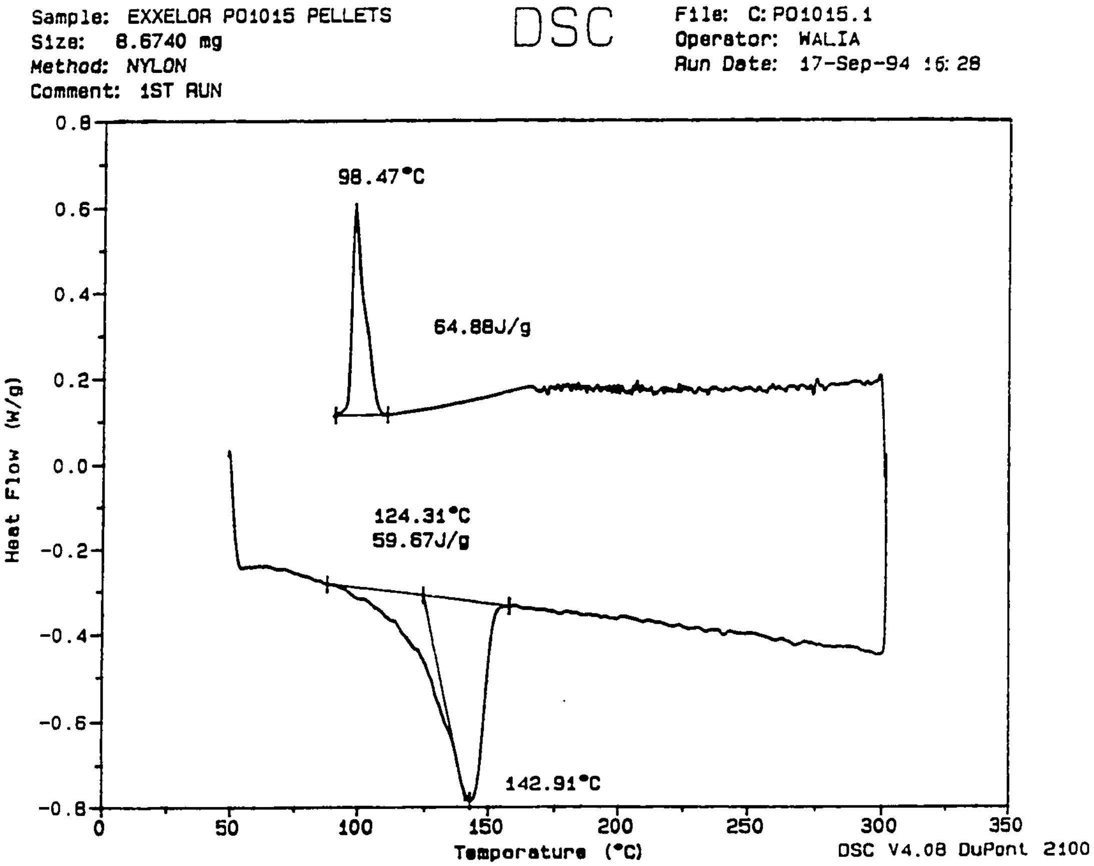


FIGURE A.41: DSC Run for Pure Exxelor PO1015 Pellet

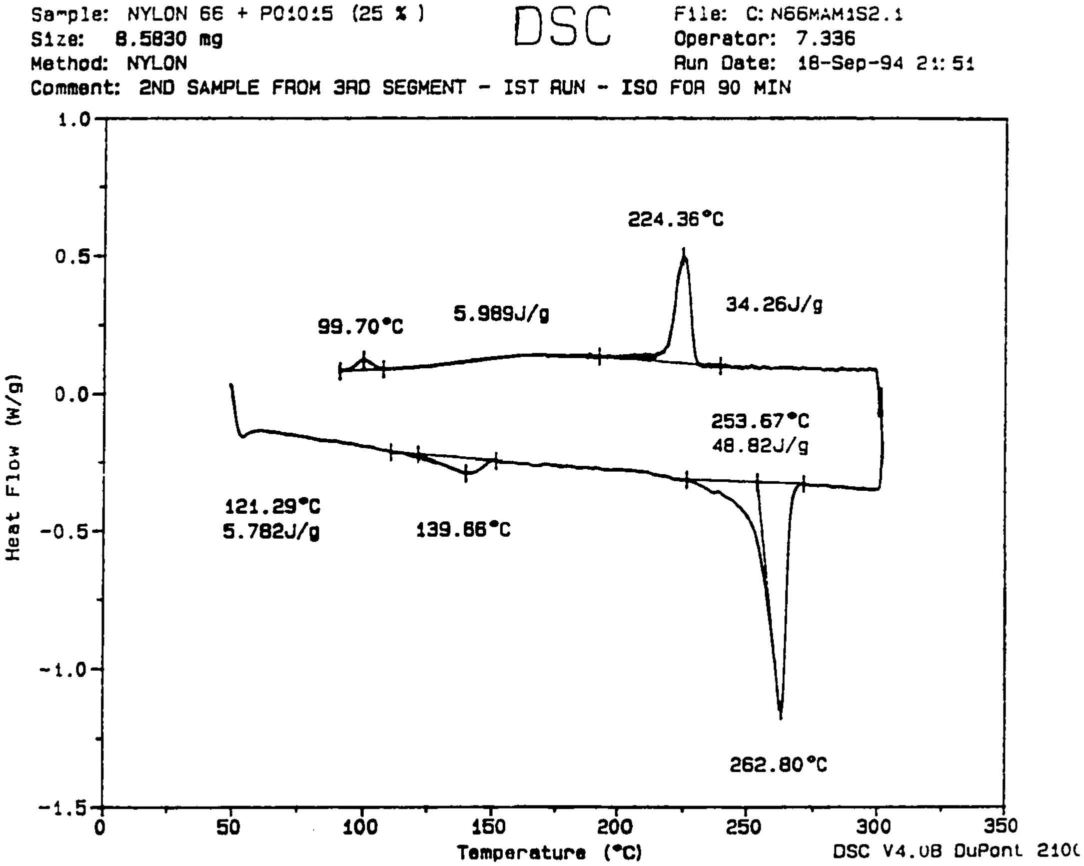


FIGURE A.42: First Run for a Nylon 6,6/Exxelor PO1015 (25% Melt Blend), Isothermal at 300°C for 90 mins

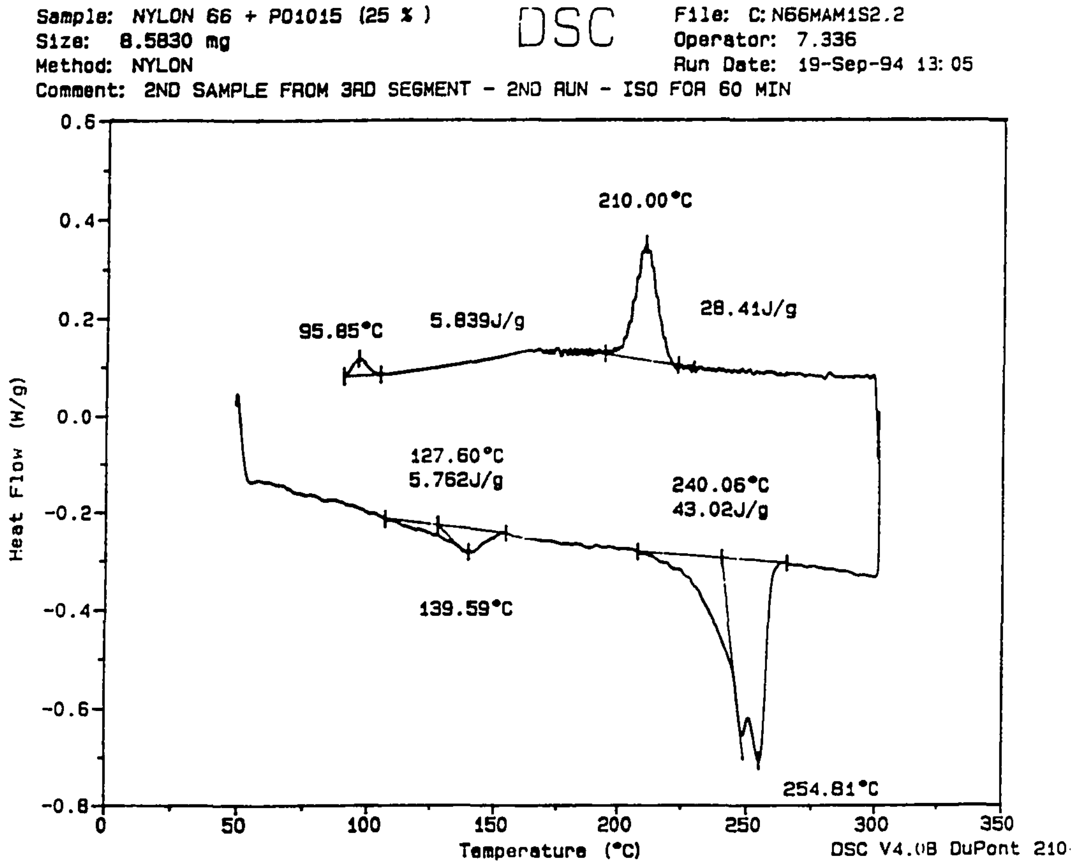


FIGURE A.43: Second Run for a Nylon 6,6/Exxelor PO1015 (25% Melt Blend), Isothermal at 300°C for 60 mins

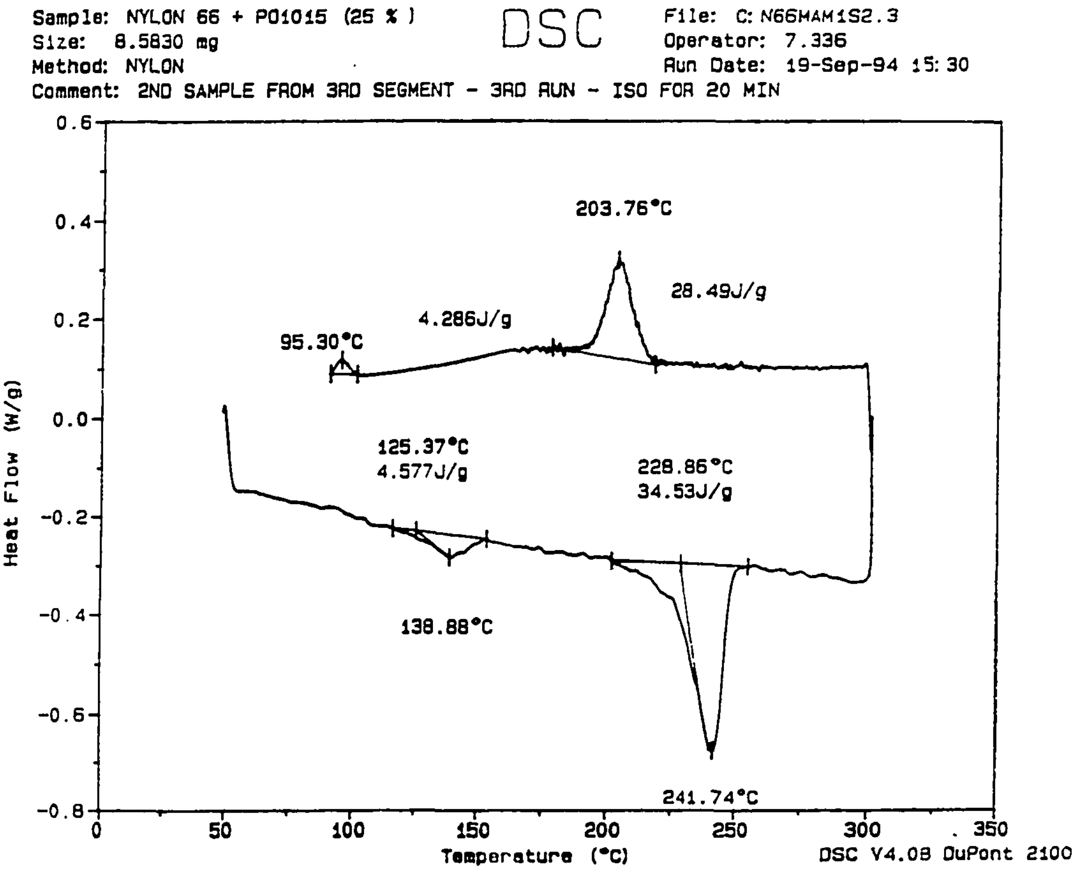
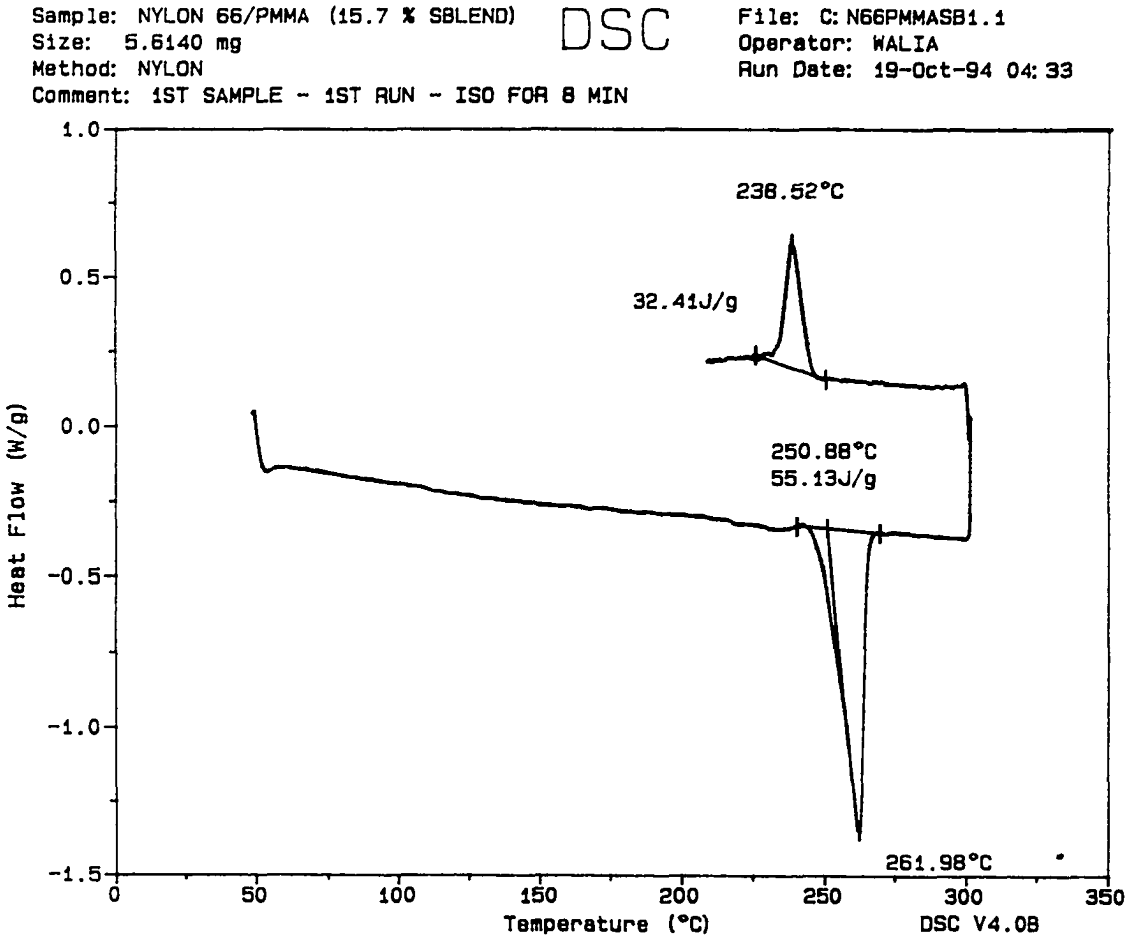


FIGURE A.44: Third Run for a Nylon 6,6/Exxelor PO1015 (25% Melt Blend), Isothermal at 300°C for 20 mins



Sample: NYLON 66/PMMA (15.7 % SBLEND)
Size: 5.6140 mg
Method: NYLON
Comment: 1ST SAMPLE - 1ST RUN - ISO FOR 8 MIN

File: C: N66PMMASB1.1
Operator: WALIA
Run Date: 19-Oct-94 04: 33

FIGURE A.45: First Run for a Nylon 6,6/Polymethylmethacrylate (15% Solution Blend), Unannealed

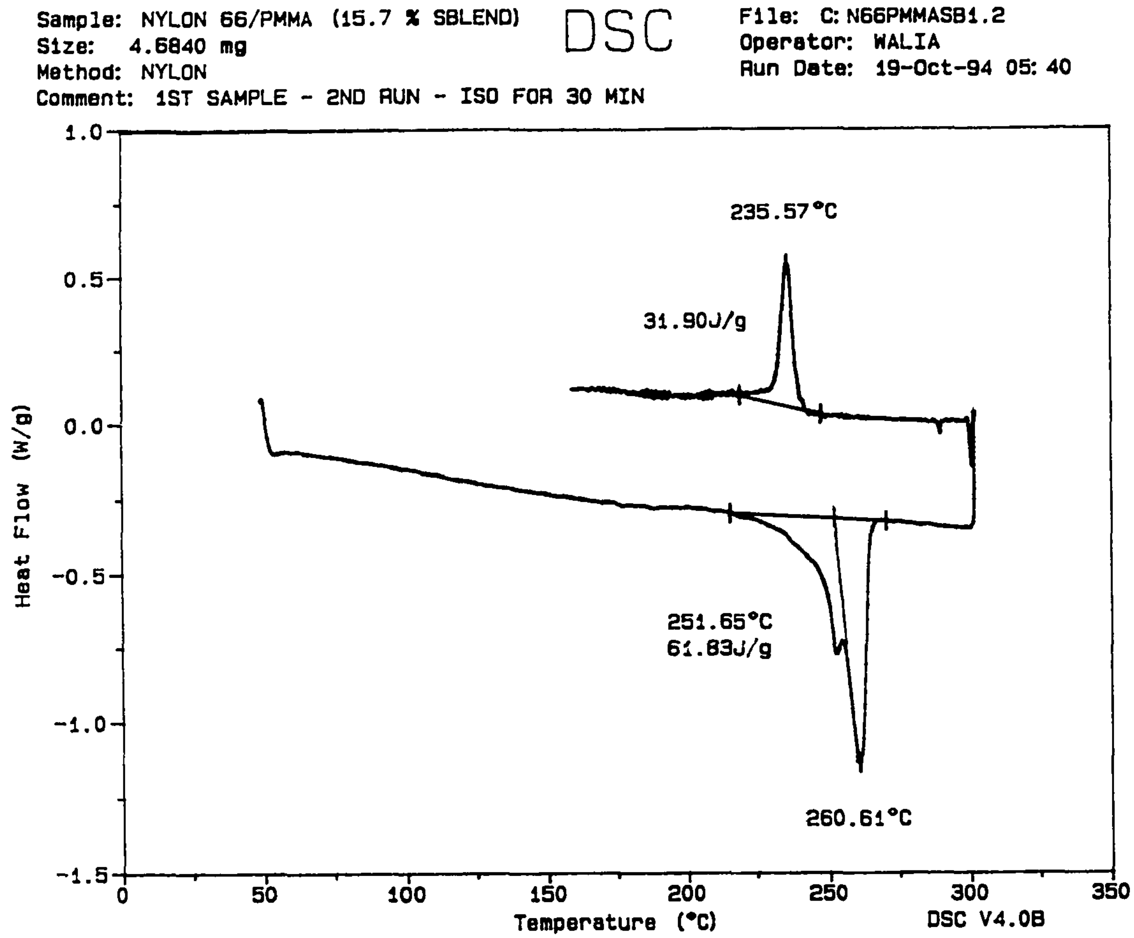


FIGURE A.46: Second Run for a Nylon 6,6/Polymethylmethacrylate (15% Solution Blend, Annealed at 300°C for 30 mins

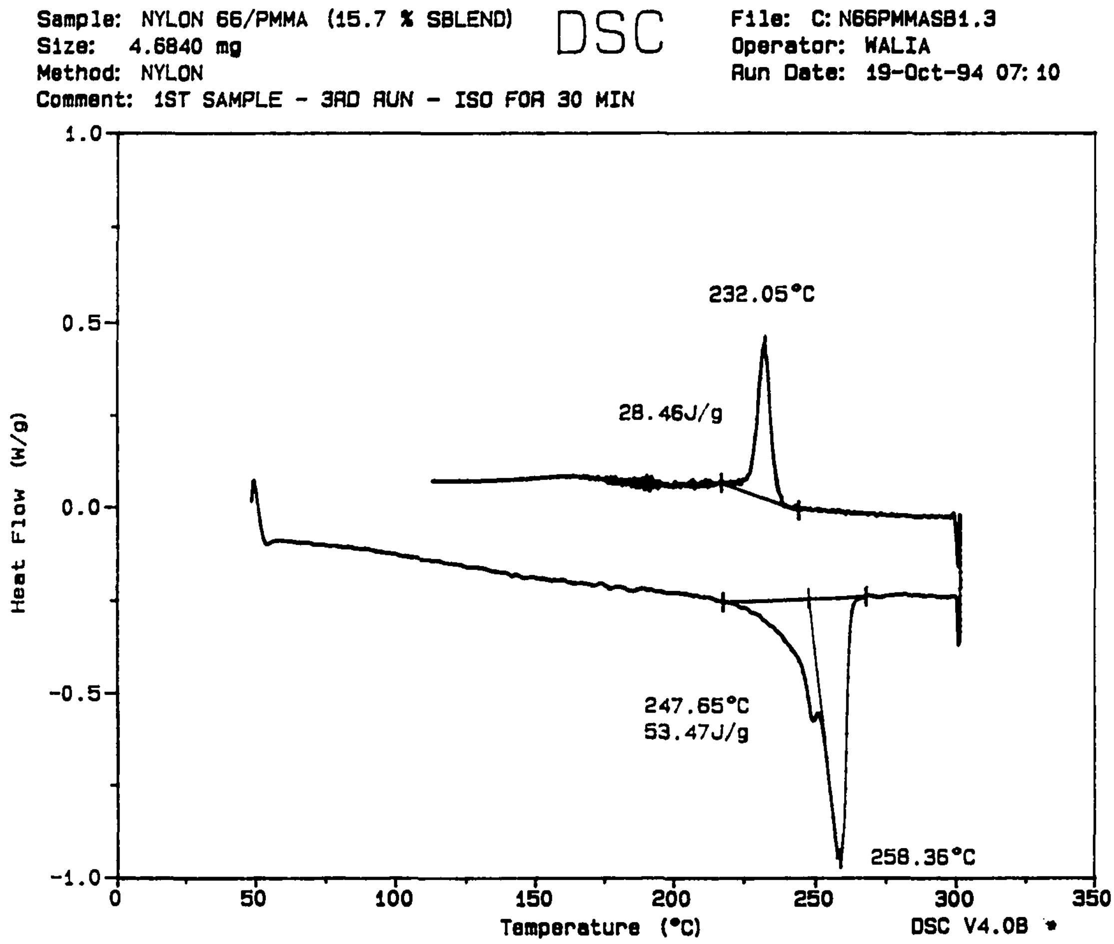


FIGURE A.47: Third Run for a Nylon 6,6/Polymethylmethacrylate (15% Solution Blend, Annealed at 300°C for 60 mins

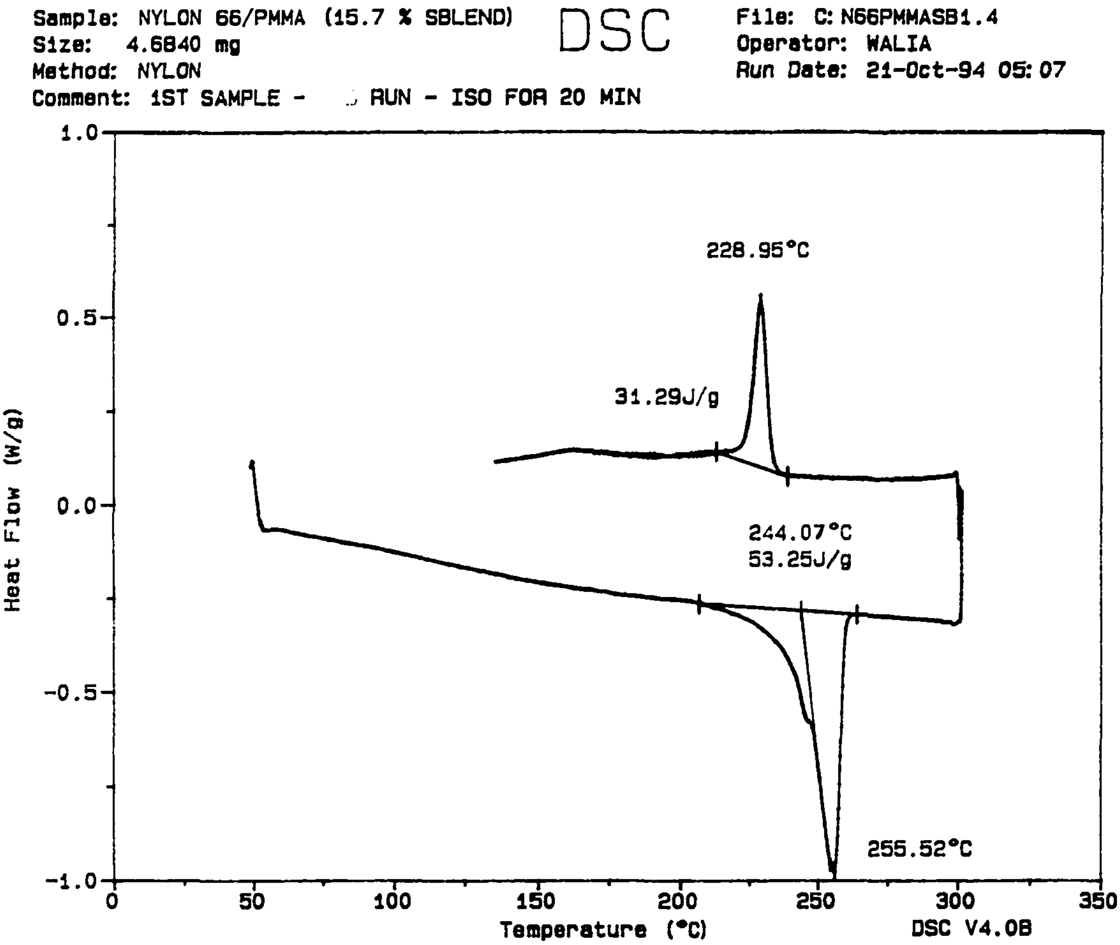


FIGURE A.48: Fourth Run for a Nylon 6,6/Polymethylmethacrylate (15% Solution Blend, Annealed at 300°C for 80 mins

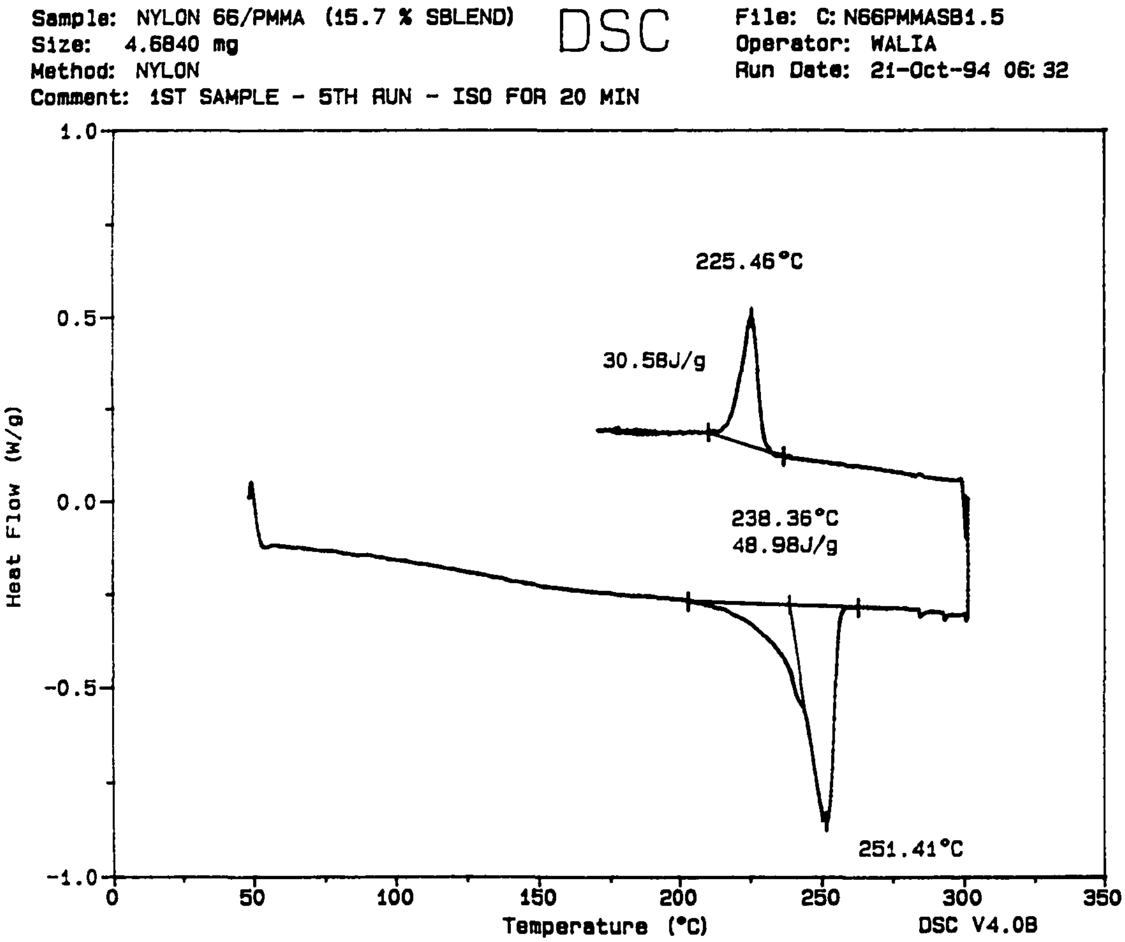


FIGURE A.49: Fifth Run for a Nylon 6,6/Polymethylmethacrylate (15% Solution Blend, Annealed at 300°C for 100 mins

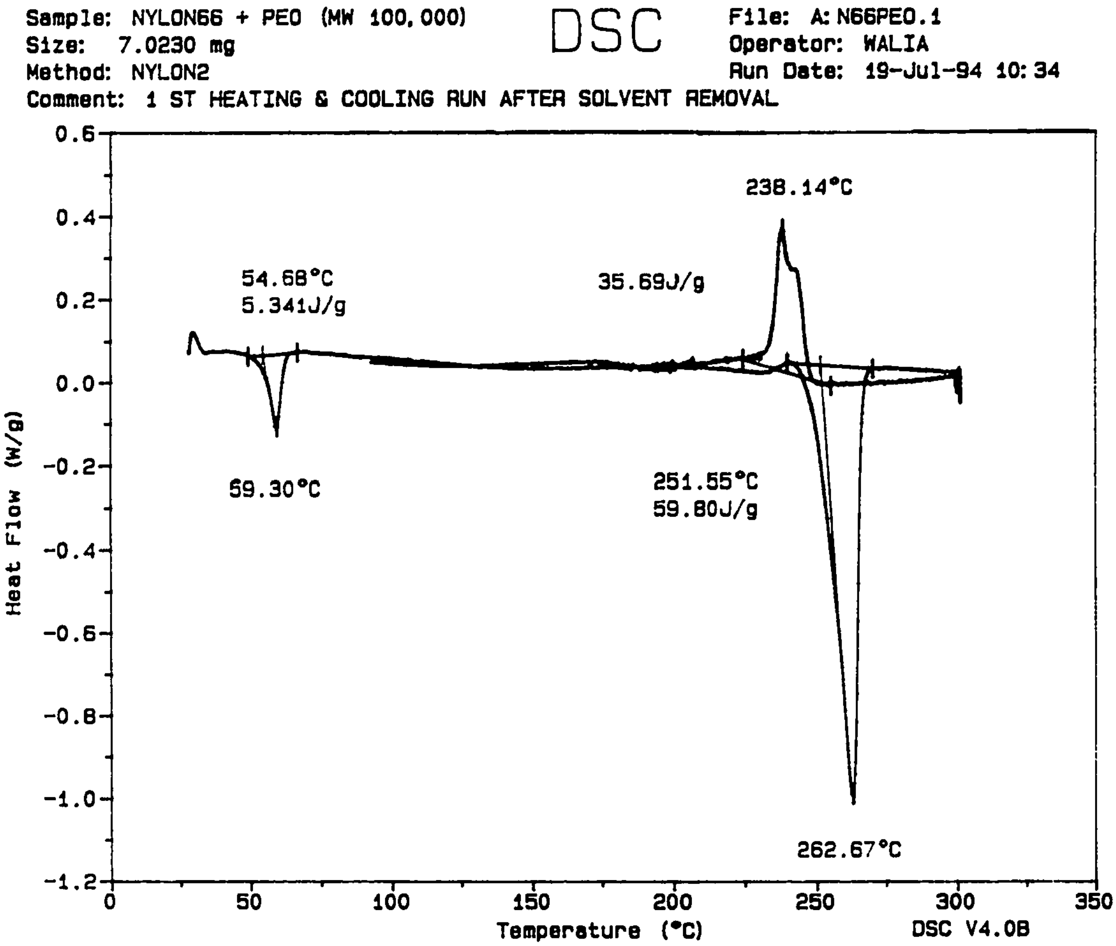


FIGURE A.50: First Run for a Nylon 6,6/Polyethylene Oxide (15% Solution Blend, Unannealed

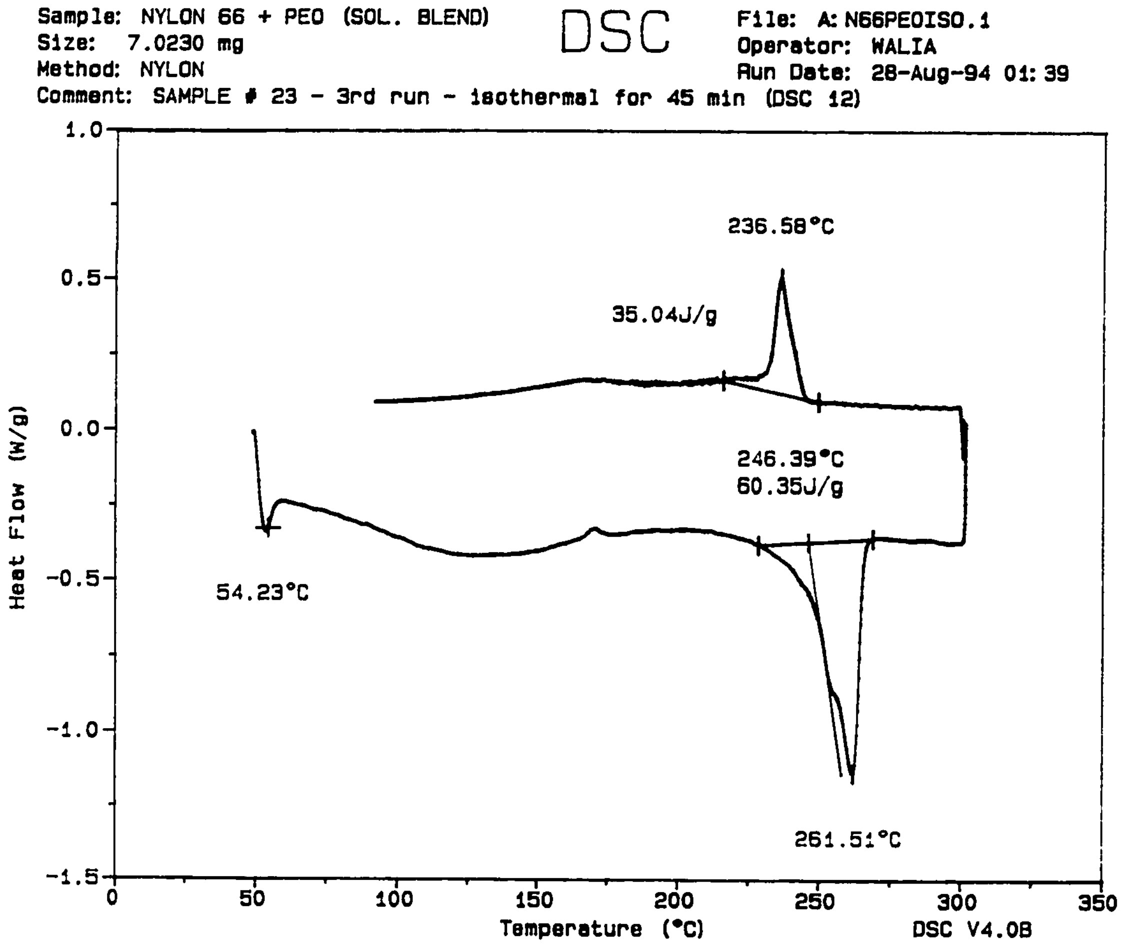
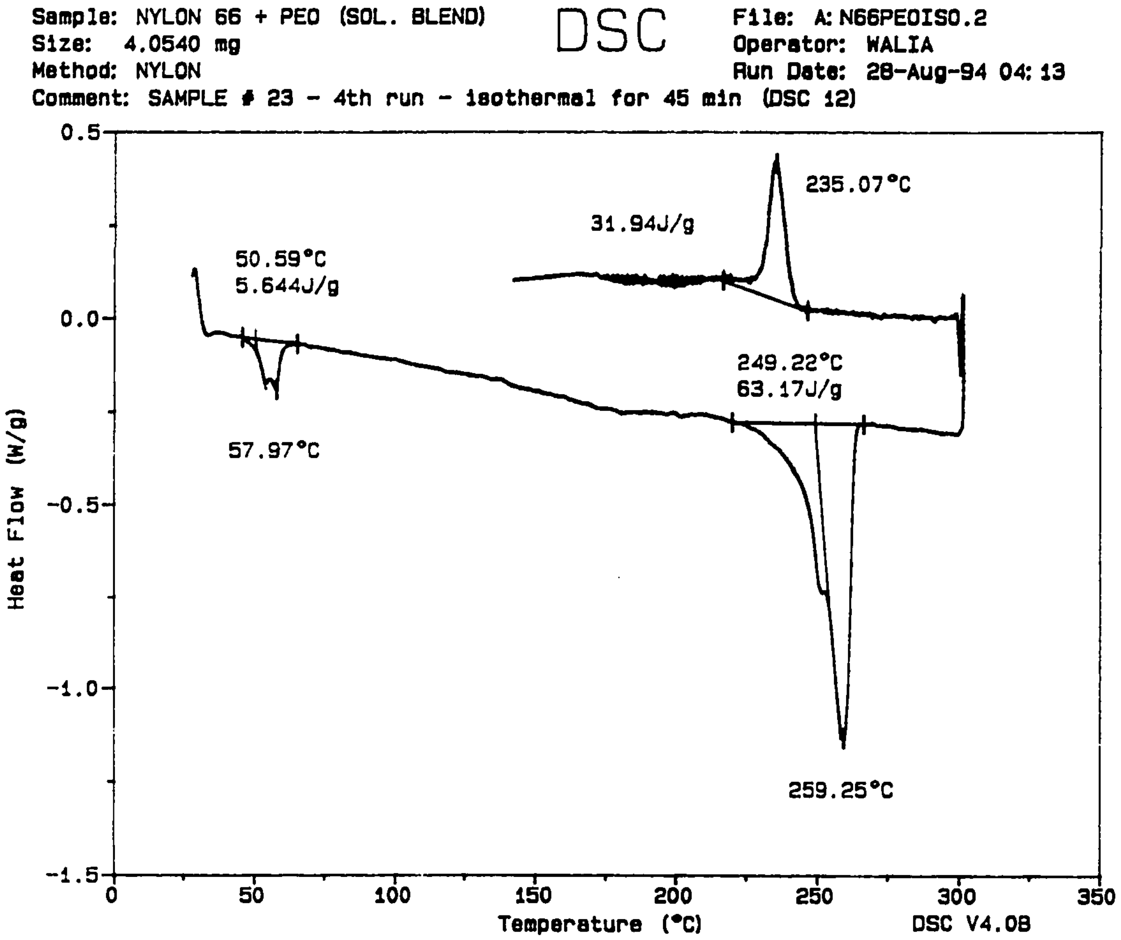


FIGURE A.51: DSC Run for a Nylon 6,6/Polyethylene Oxide (15% Solution Blend, Annealed at 300°C for 45 mins



Sample: NYLON 66 + PEO (SOL. BLEND)
Size: 4.0540 mg
Method: NYLON
Comment: SAMPLE # 23 - 4th run - isothermal for 45 min (DSC 12)

File: A:N66PEOISO.2
Operator: WALIA
Run Date: 28-Aug-94 04:13

FIGURE A.52: DSC Run for a Nylon 6,6/Polyethylene Oxide (15% Solution Blend, Annealed at 300°C for 90 mins

APPENDIX B

DSC NON-ISOTHERMAL RUNS OF THE DETAILED EXPERIMENTATION STAGE

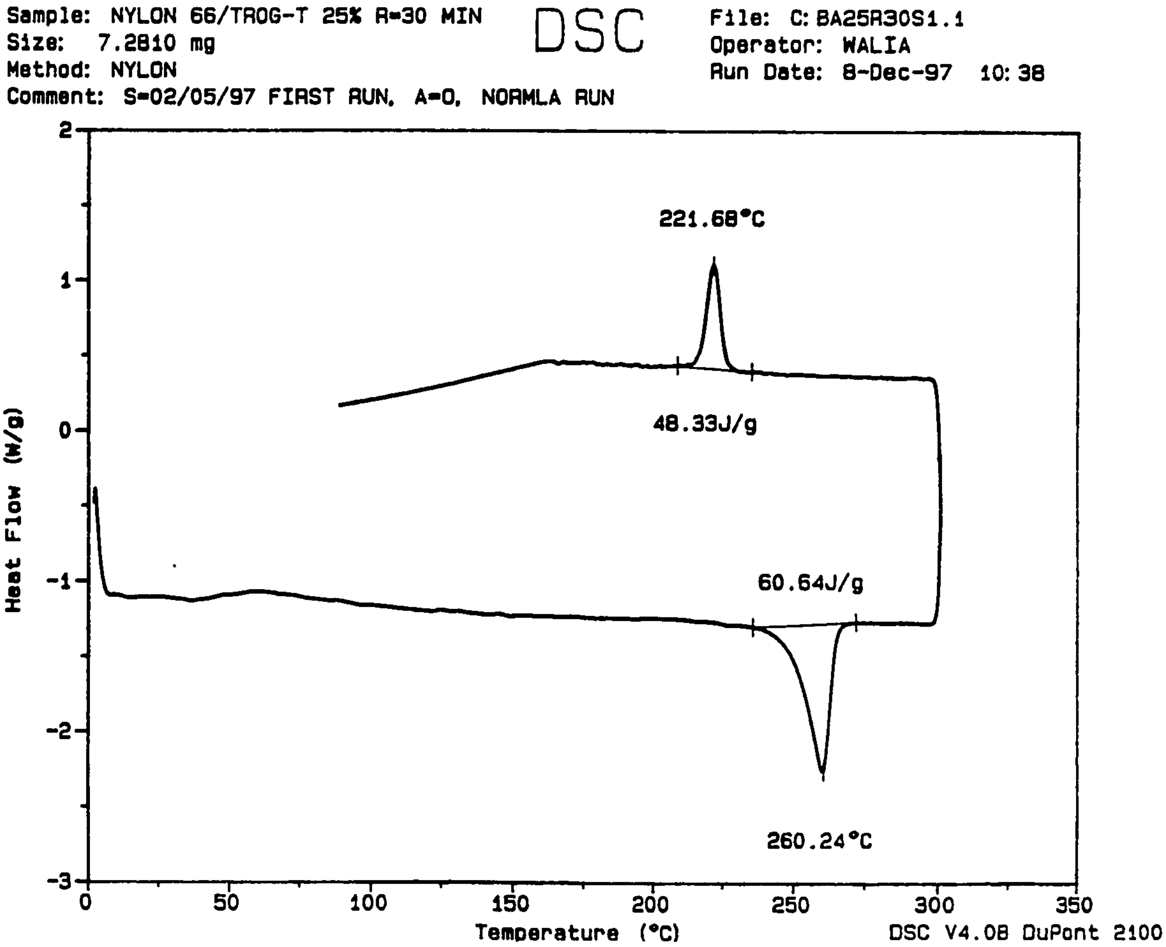


FIGURE B.1: DSC Run for 25% Nylon 6,6/Trogamid-T, RT=5 min Blend, Unannealed (A=0)

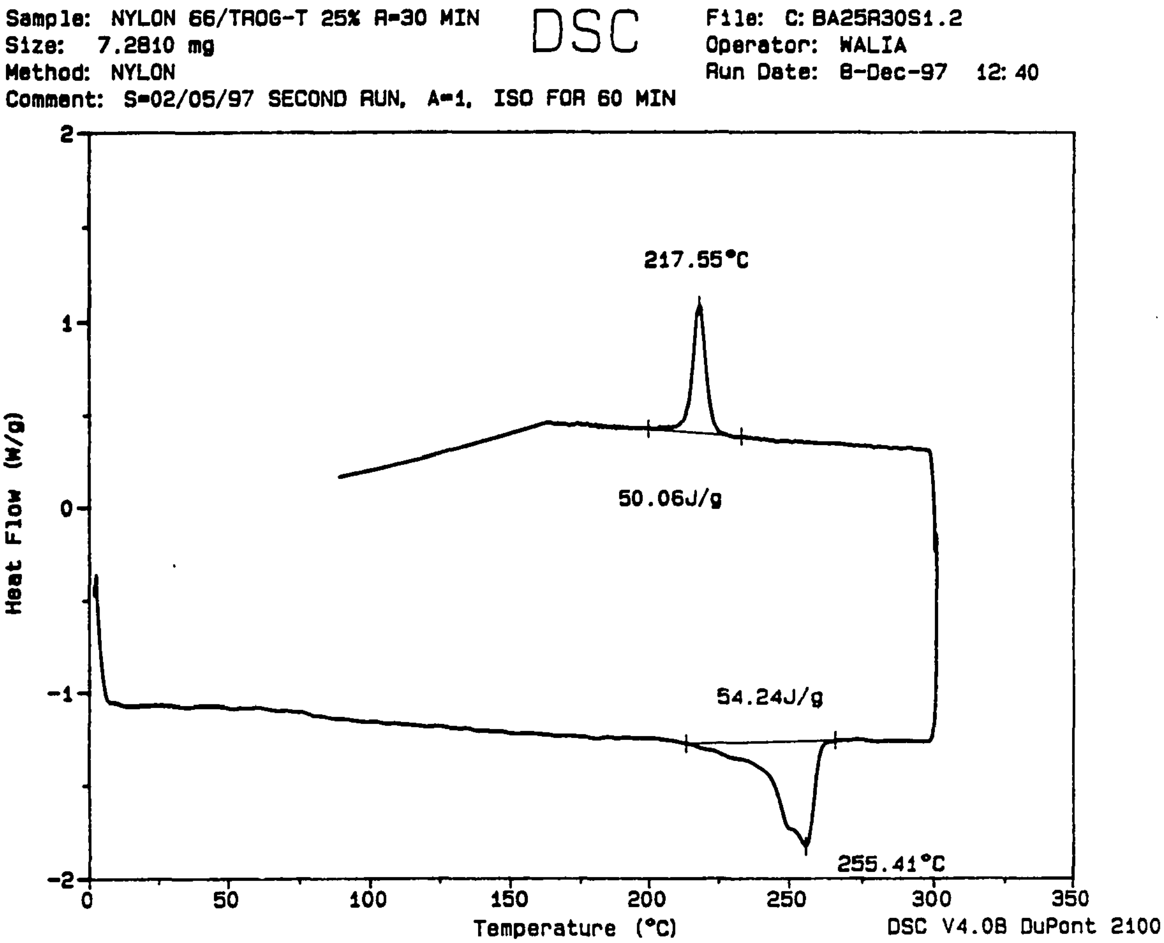


FIGURE B.2: DSC Run for 25% Nylon 6,6/Trogamid-T, RT=5 min Blend, Annealed for 1 hr (A=1)

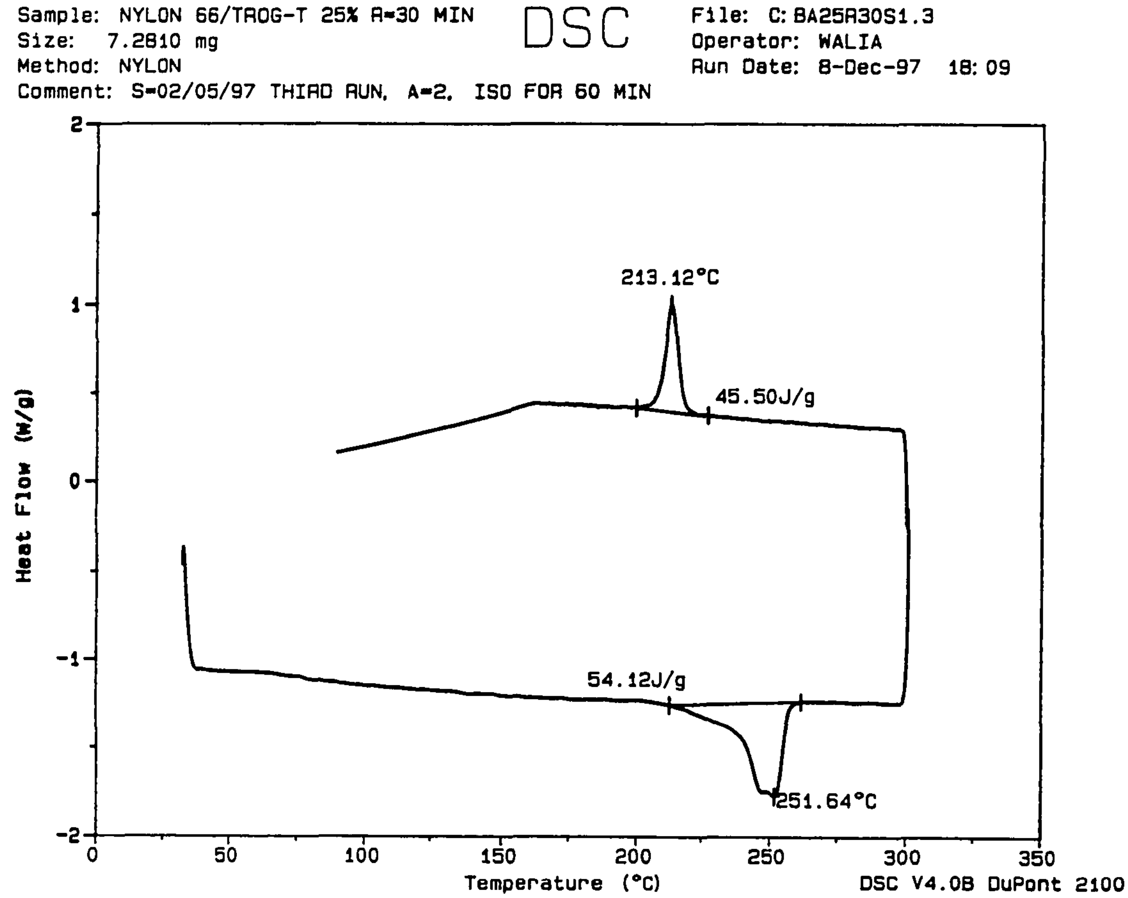


FIGURE B.3: DSC Run for 25% Nylon 6,6/Trogamid-T, RT=5 min Blend, Annealed for 2 hrs (A=2)

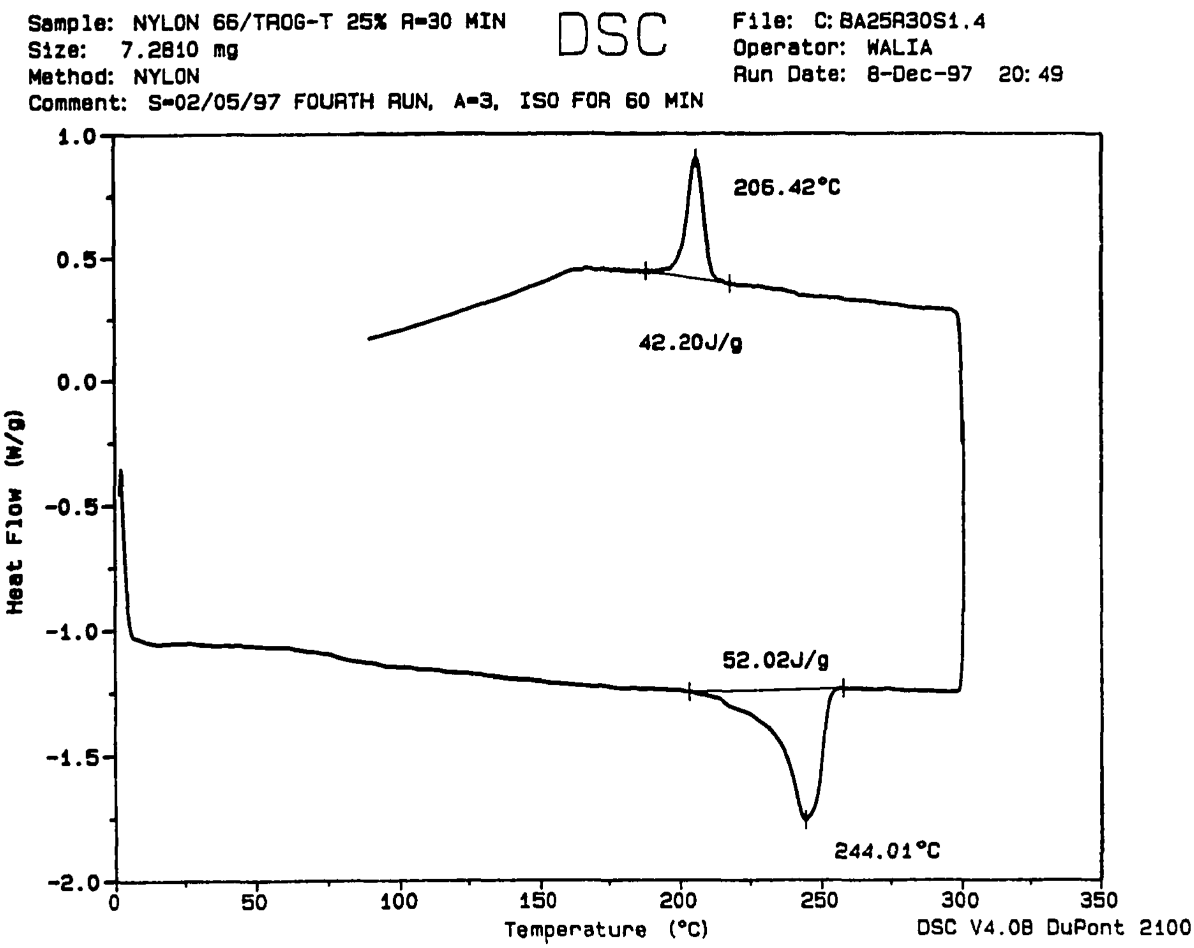


FIGURE B.4: DSC Run for 25% Nylon 6,6/Trogamid-T, RT=5 min Blend, Annealed for 3 hrs (A=3)

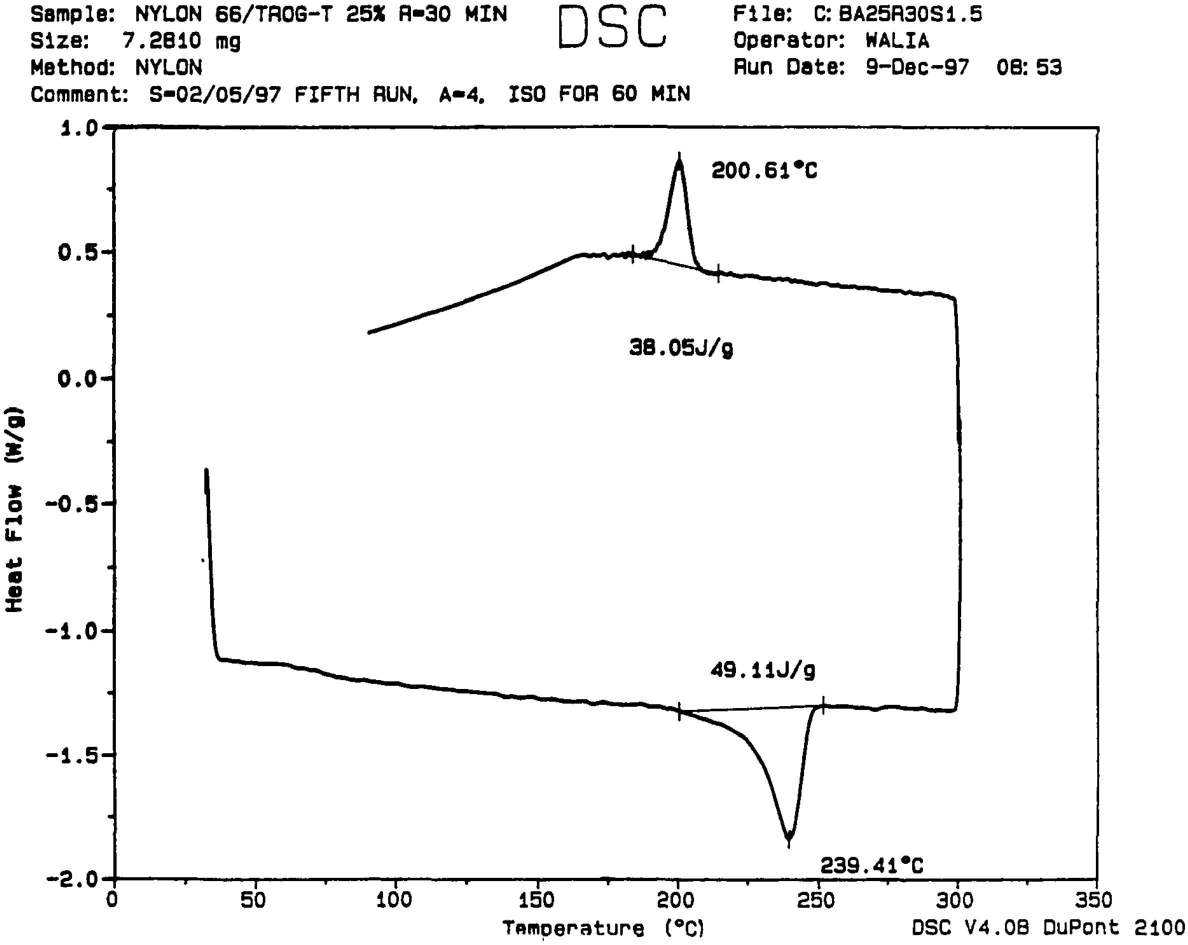


FIGURE B.5: DSC Run for 25% Nylon 6,6/Trogamid-T, RT=5 min Blend, Annealed for 4 hrs (A=4)

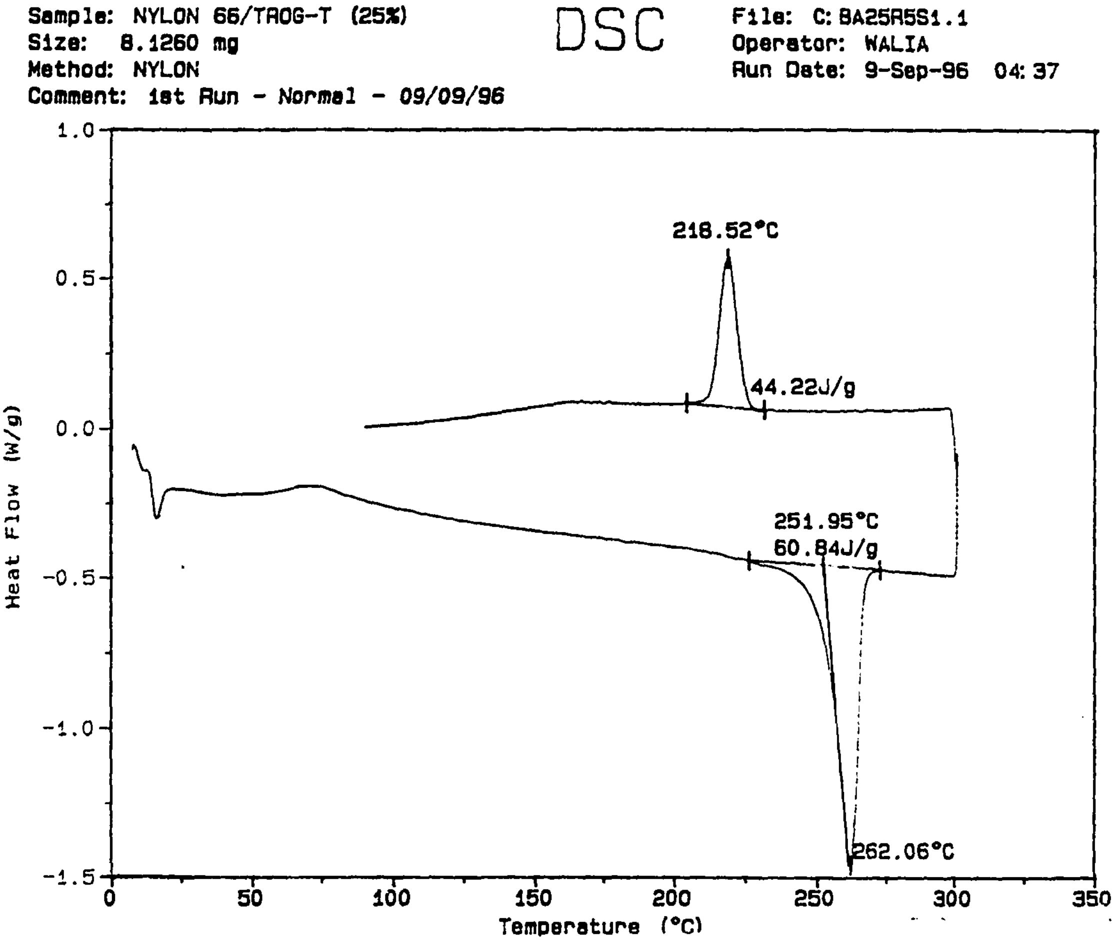


FIGURE B.6: DSC Run for 25% Nylon 6,6/Trogamid-T, RT=30 min Blend, Unannealed (A=0)

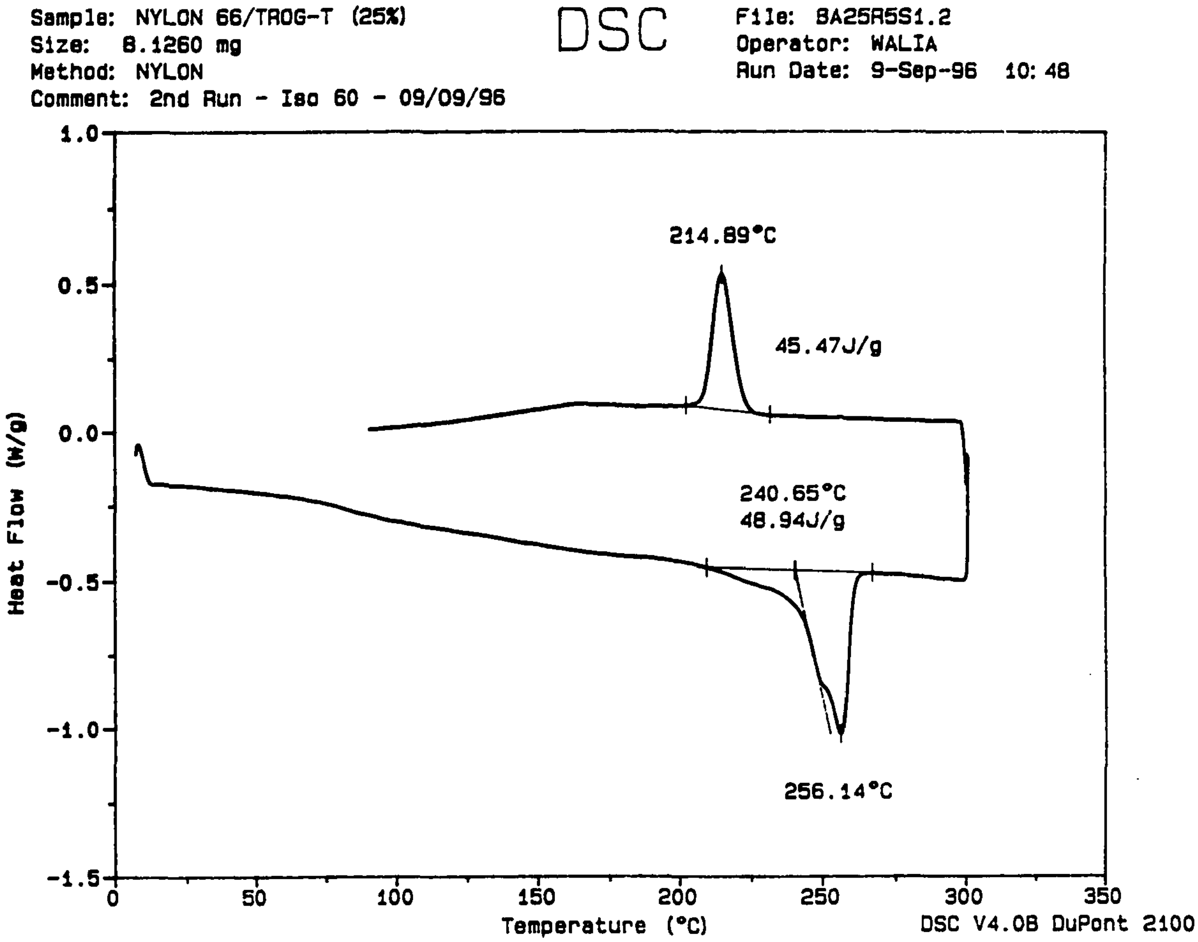


FIGURE B.7: DSC Run for 25% Nylon 6,6/Trogamid-T, RT=30 min Blend, Annealed for 1 hr (A=1)

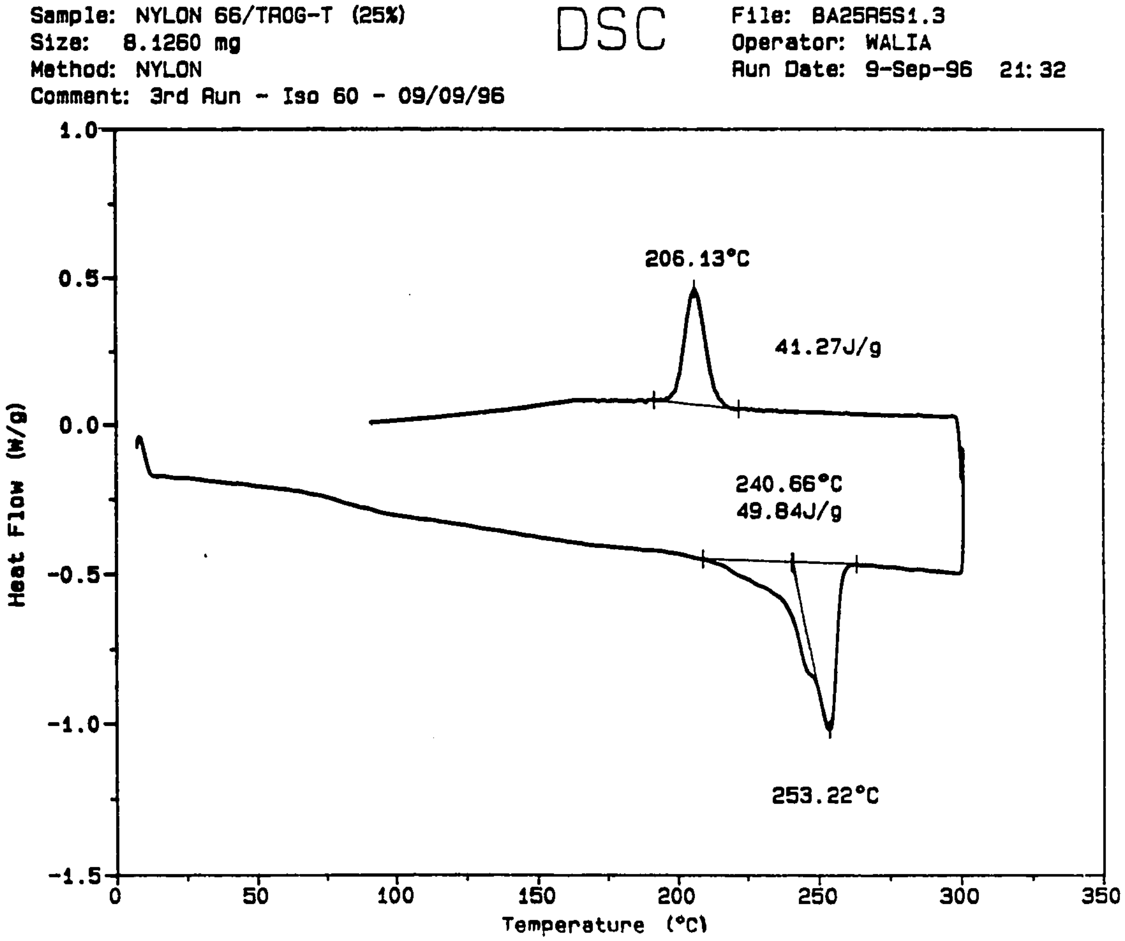


FIGURE B.8: DSC Run for 25% Nylon 6,6/Trogamid-T, RT=30 min Blend, Annealed for 2 hrs (A=2)

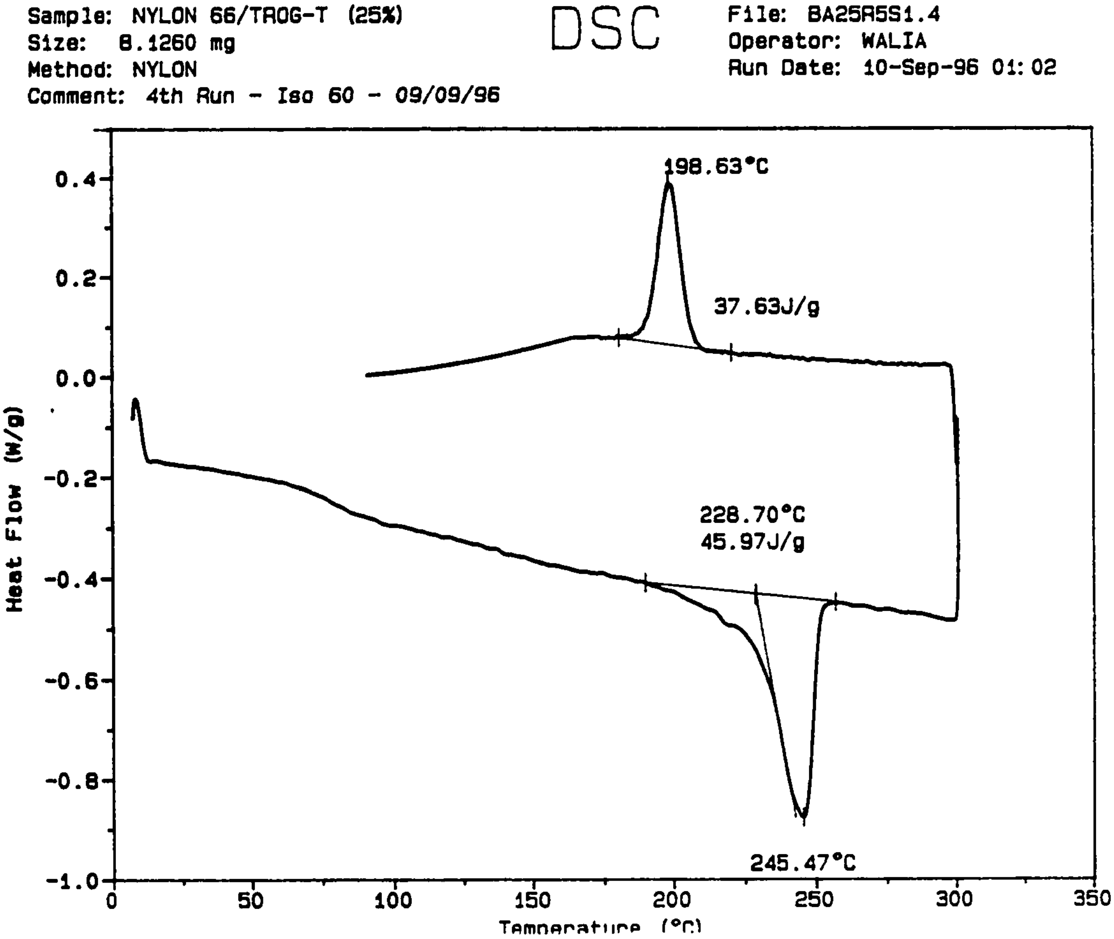


FIGURE B.9: DSC Run for 25% Nylon 6,6/Trogamid-T, RT=30 min Blend, Annealed for 3 hrs (A=3)

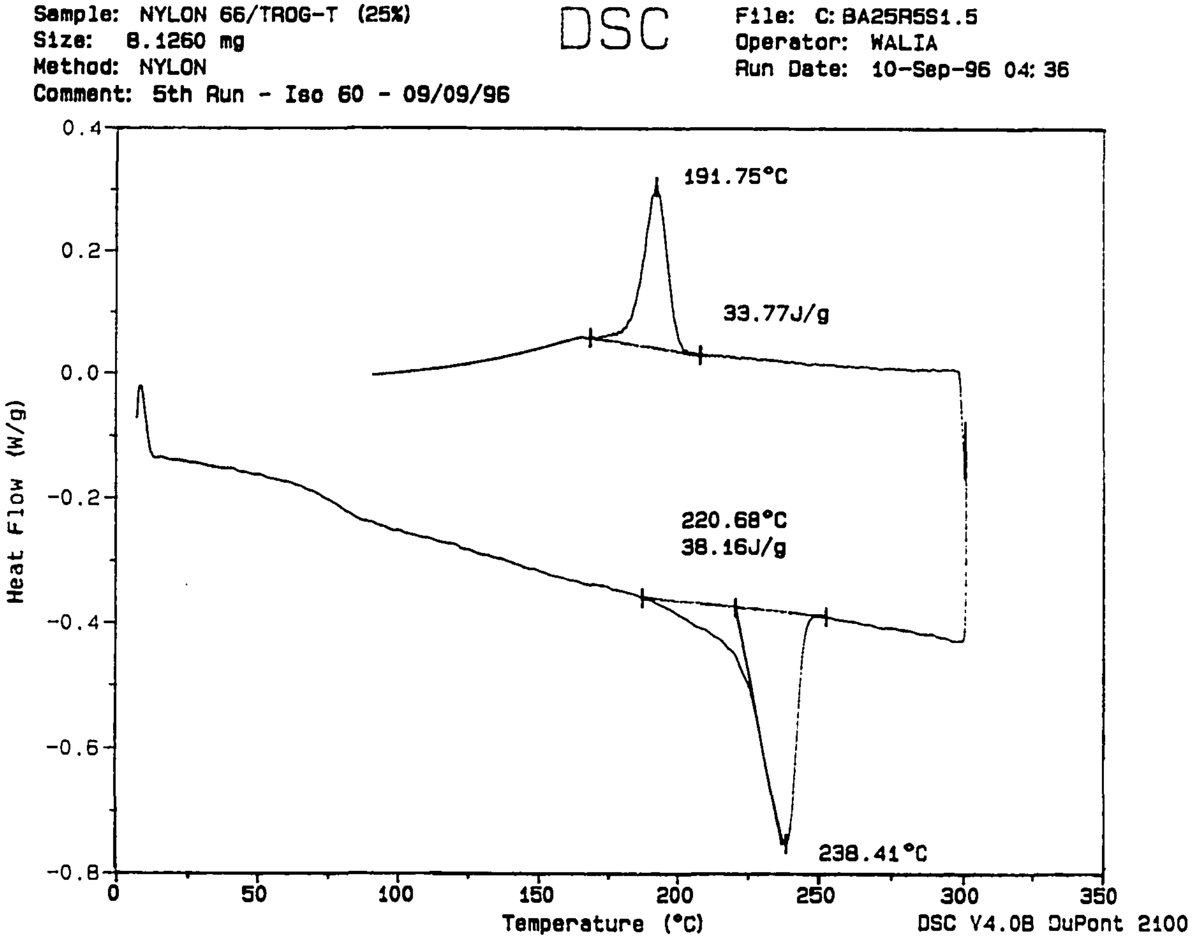


FIGURE B.10: DSC Run for 25% Nylon 6,6/Trogamid-T, RT=30 min Blend, Annealed for 4 hrs (A=4)

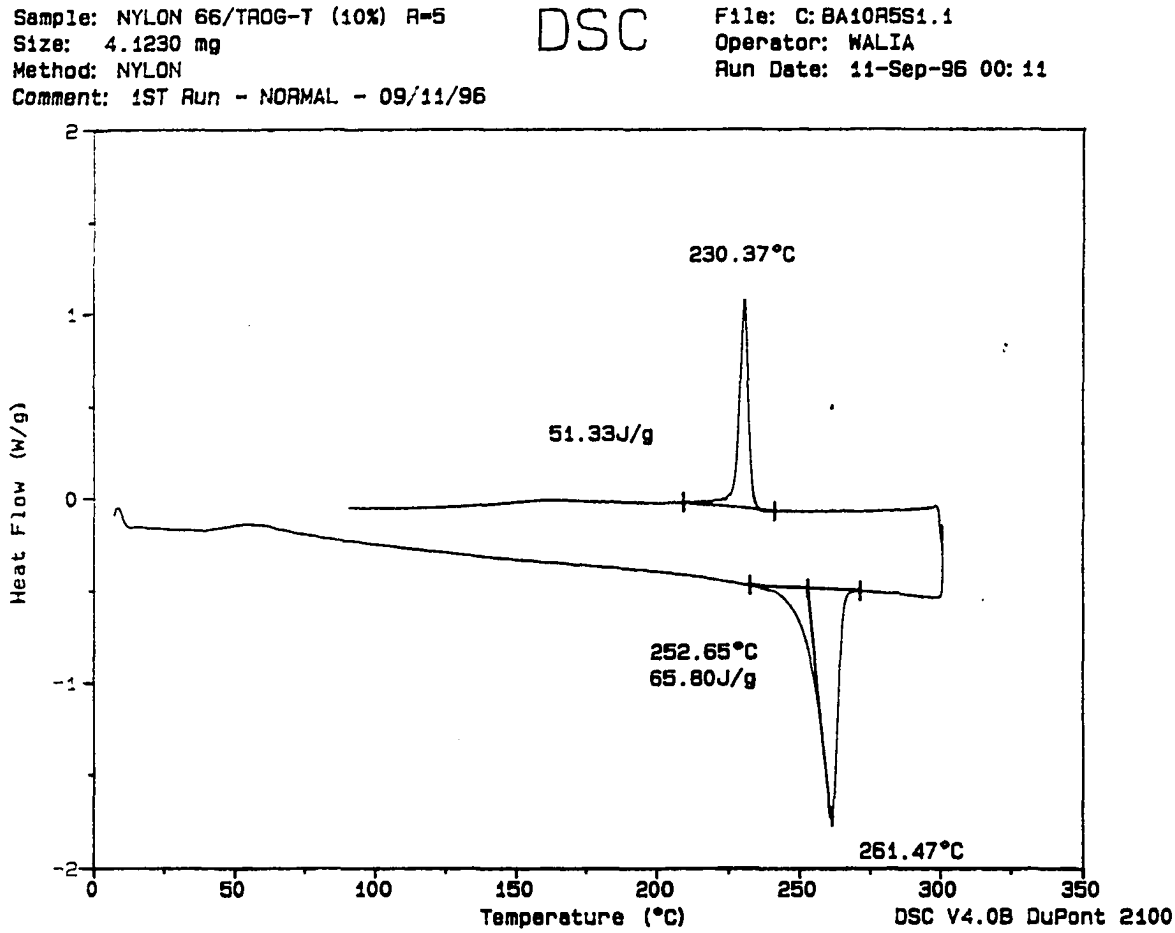


FIGURE B.11: DSC Run for 10% Nylon 6,6/Trogamid-T, RT=5 min Blend, Unannealed (A=0)

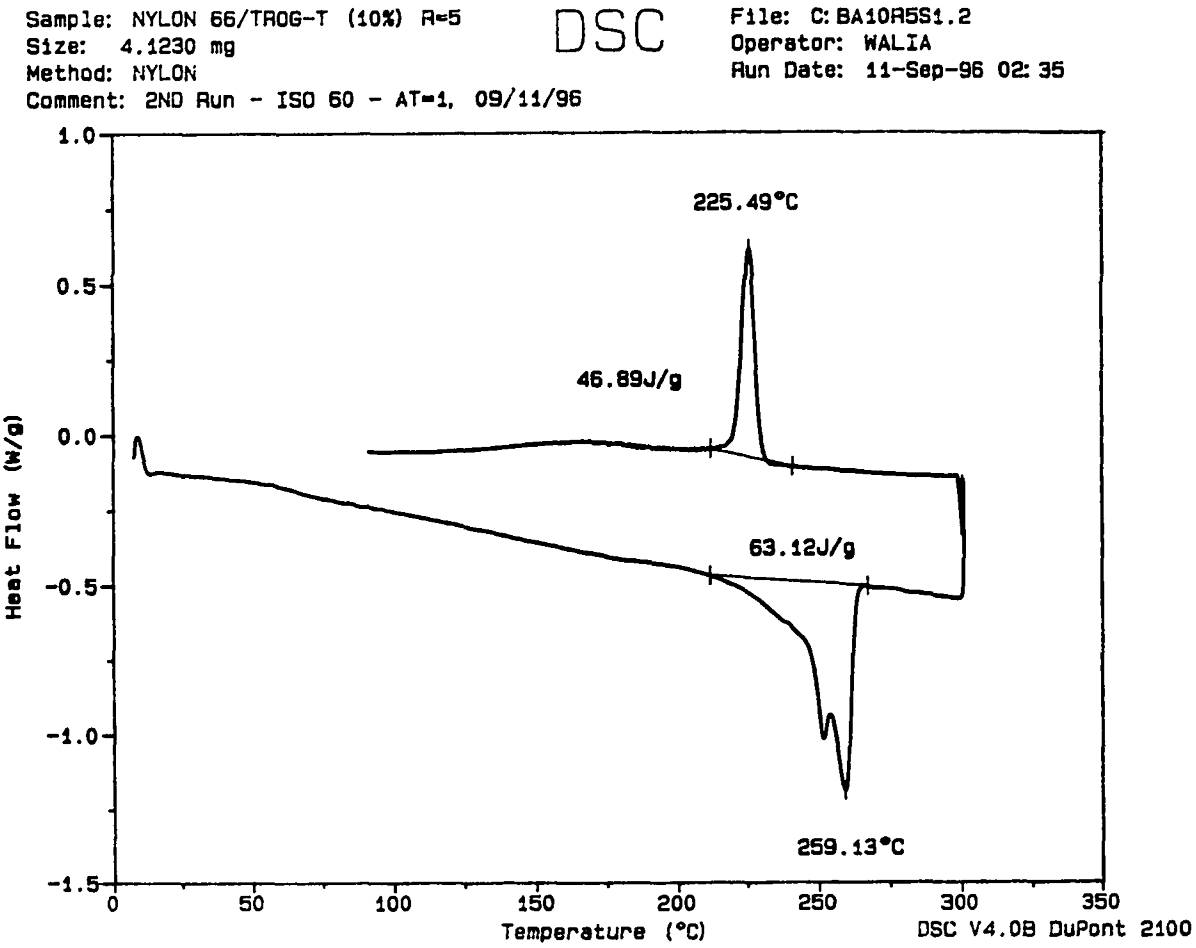
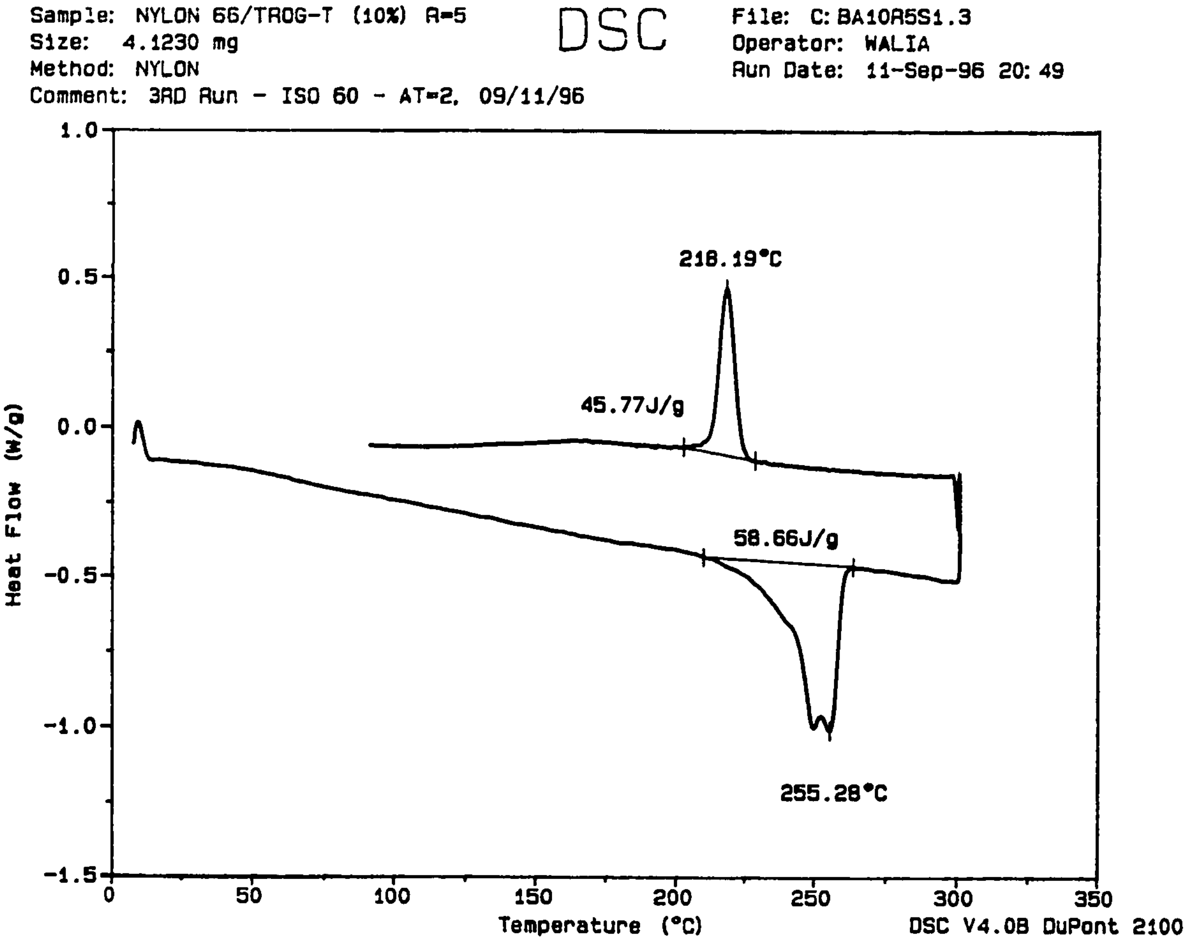


FIGURE B.12: DSC Run for 10% Nylon 6,6/Trogamid-T, RT=5 min Blend, Annealed for 1 hr (A=1)



Sample: NYLON 66/TROG-T (10%) R=5
Size: 4.1230 mg
Method: NYLON
Comment: 3RD Run - ISO 60 - AT=2, 09/11/96

File: C:BA10R5S1.3
Operator: WALIA
Run Date: 11-Sep-96 20:49

FIGURE B.13: DSC Run for 10% Nylon 6,6/Trogamid-T, RT=5 min Blend, Annealed for 2 hr (A=2)

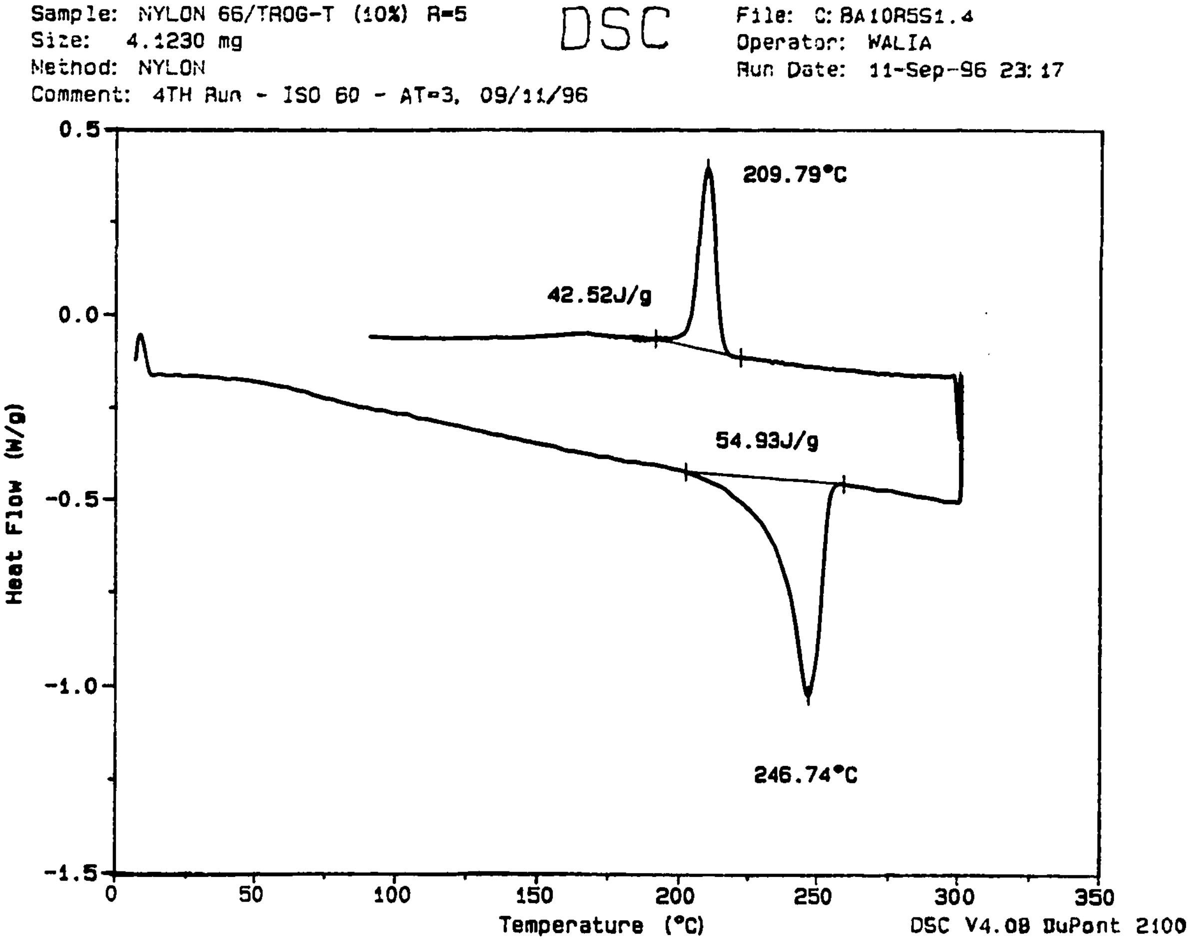
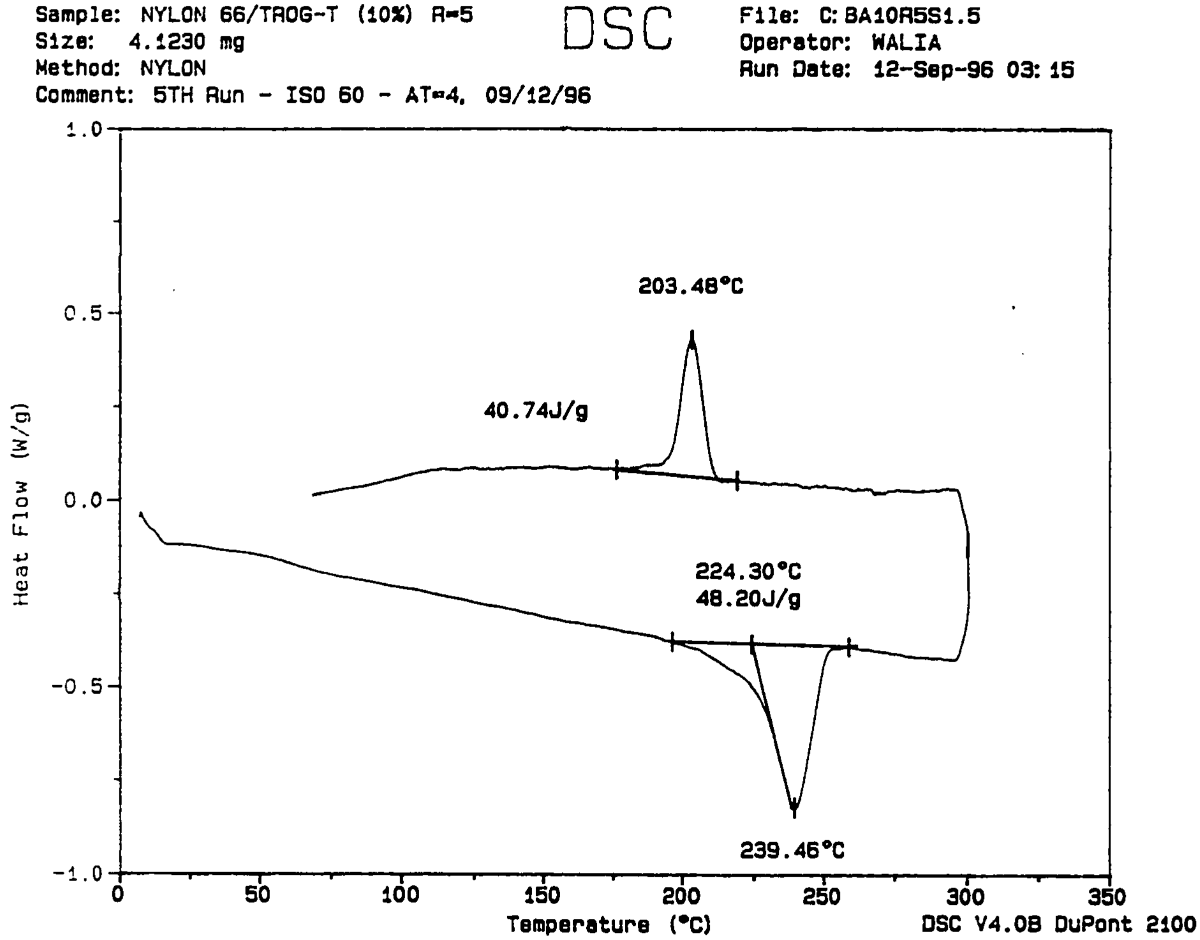


FIGURE B.14: DSC Run for 10% Nylon 6,6/Trogamid-T, RT=5 min Blend, Annealed for 3 hr (A=3)



Sample: NYLON 66/TROG-T (10%) R=5
Size: 4.1230 mg
Method: NYLON
Comment: 5TH Run - ISO 60 - AT=4, 09/12/96

File: C:BA10R5S1.5
Operator: WALIA
Run Date: 12-Sep-96 03:15

FIGURE B.15: DSC Run for 10% Nylon 6,6/Trogamid-T, RT=5 min Blend, Annealed for 4 hr (A=4)

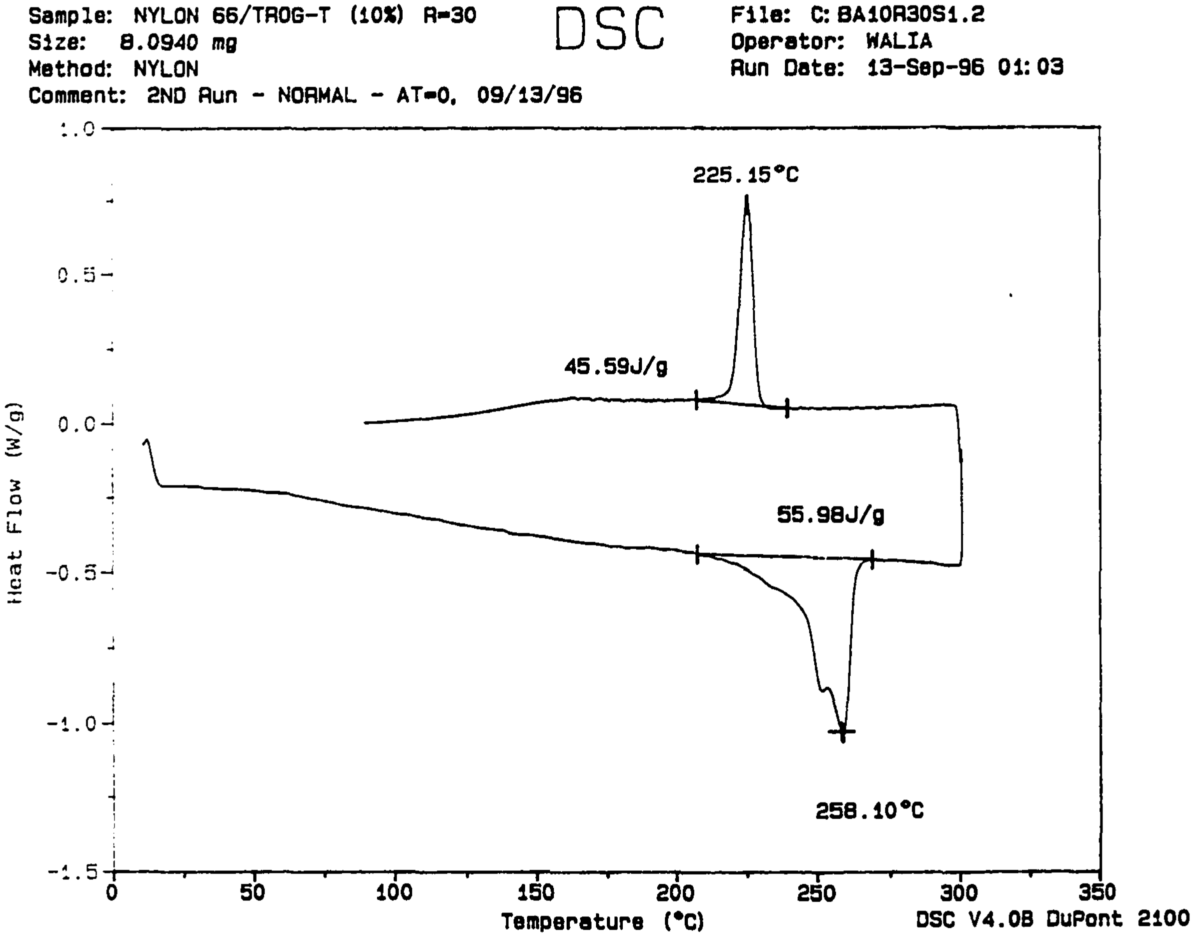


FIGURE B.16: DSC Run for 10% Nylon 6,6/Trogamid-T, RT=30 min Blend, Unannealed (A=0)

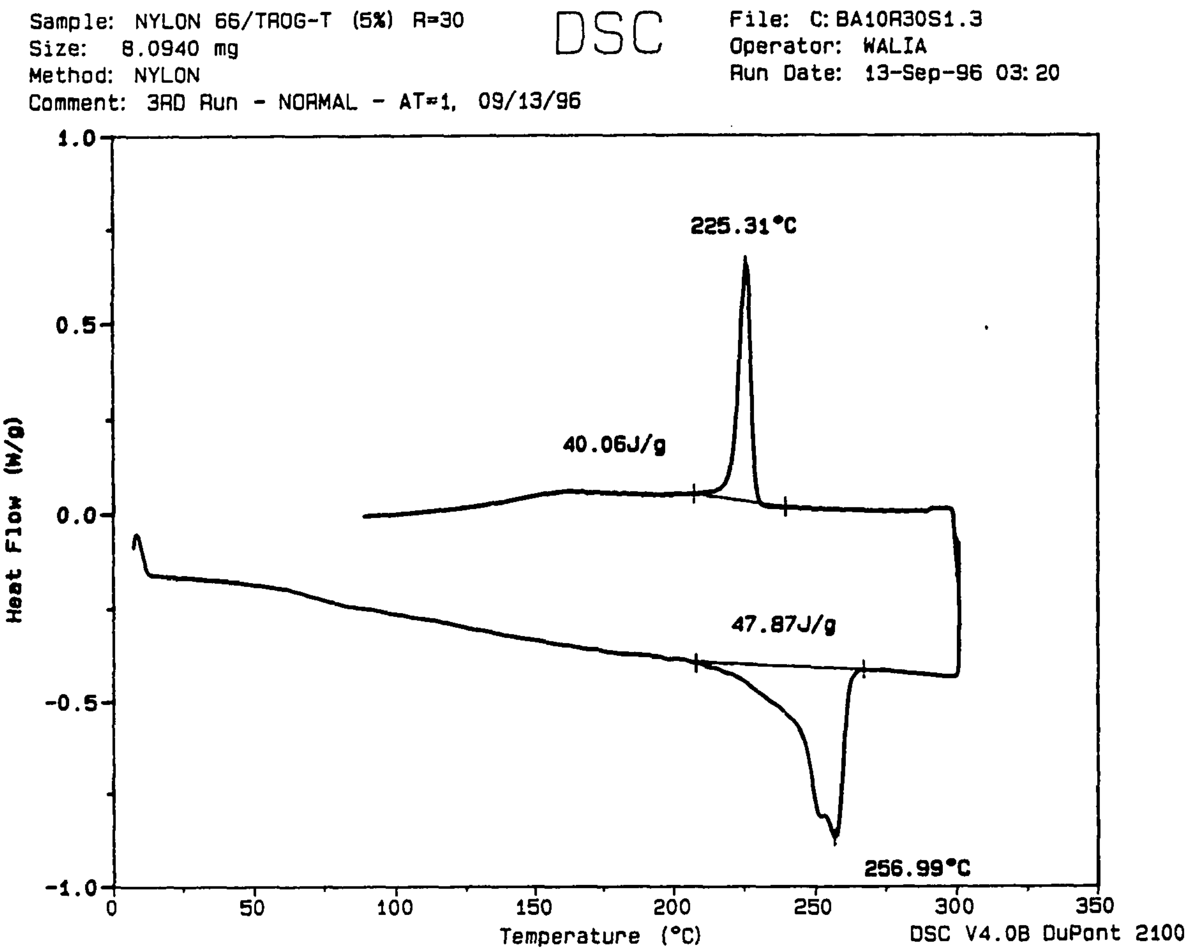


FIGURE B.17: DSC Run for 10% Nylon 6,6/Trogamid-T, RT=30 min Blend, annealed for 1 hr (A=1)

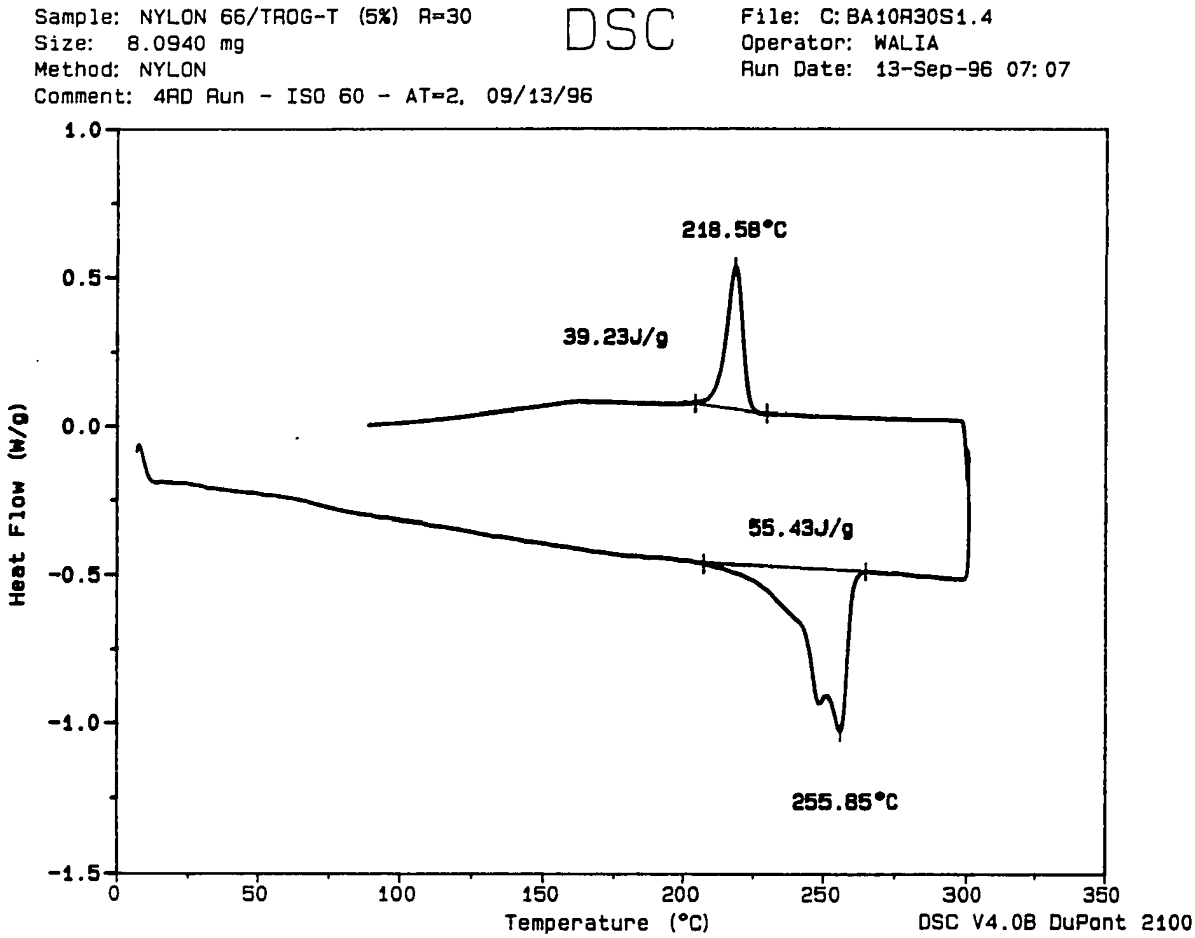


FIGURE B.18: DSC Run for 10% Nylon 6,6/Trogamid-T, RT=30 min Blend, Annealed for 2 hr (A=2)

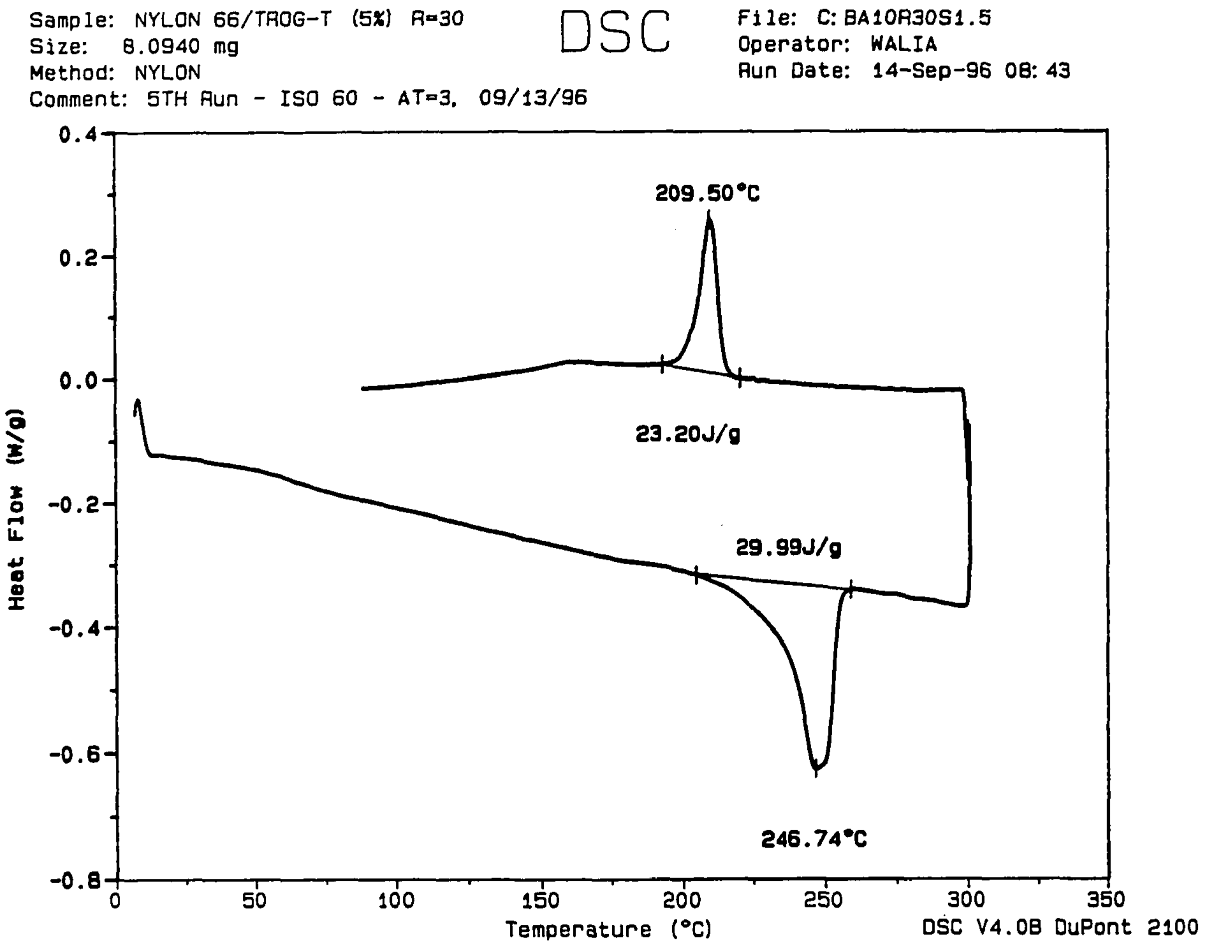


FIGURE B.19: DSC Run for 10% Nylon 6,6/Trogamid-T, RT=30 min Blend, Annealed for 3 hr (A=3)

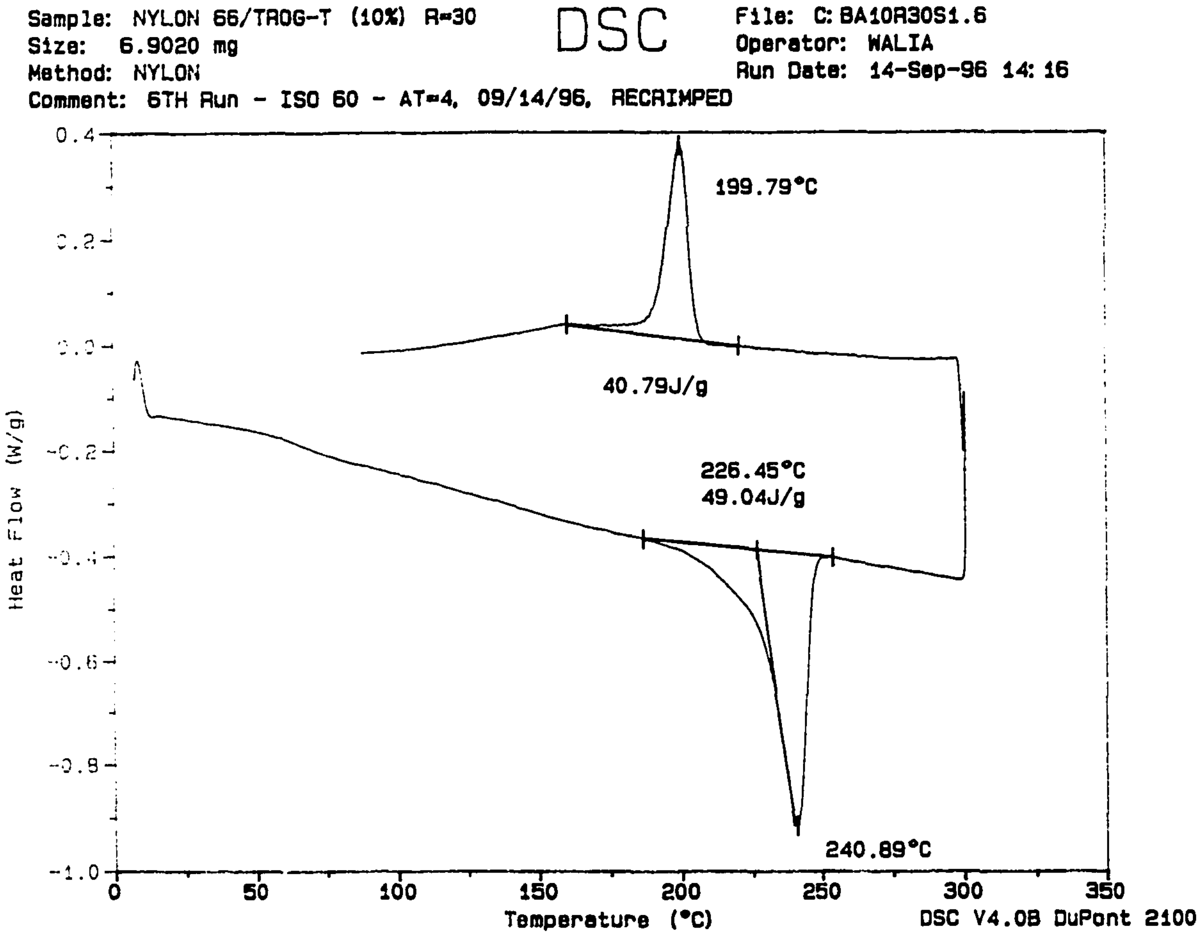
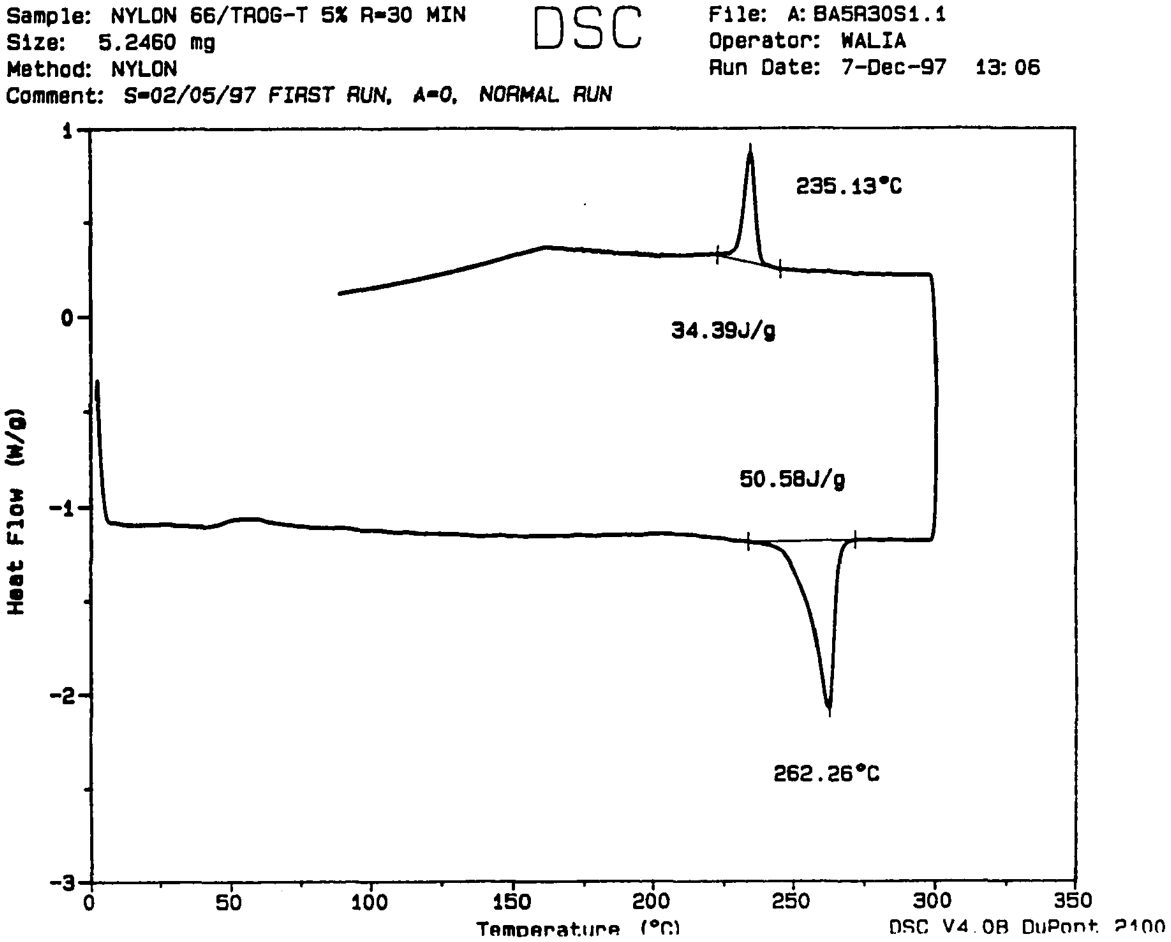


FIGURE B.20: DSC Run for 10% Nylon 6,6/Trogamid-T, RT=30 min , Annealed for 4 hr (A=4)



Sample: NYLON 66/TROG-T 5% R=30 MIN
Size: 5.2460 mg
Method: NYLON
Comment: S=02/05/97 FIRST RUN, A=0, NORMAL RUN

File: A: BA5R30S1.1
Operator: WALIA
Run Date: 7-Dec-97 13:06

FIGURE B.21: DSC Run for 5% Nylon 6,6/Trogamid-T, RT=5 min Blend, Unannealed (A=0)

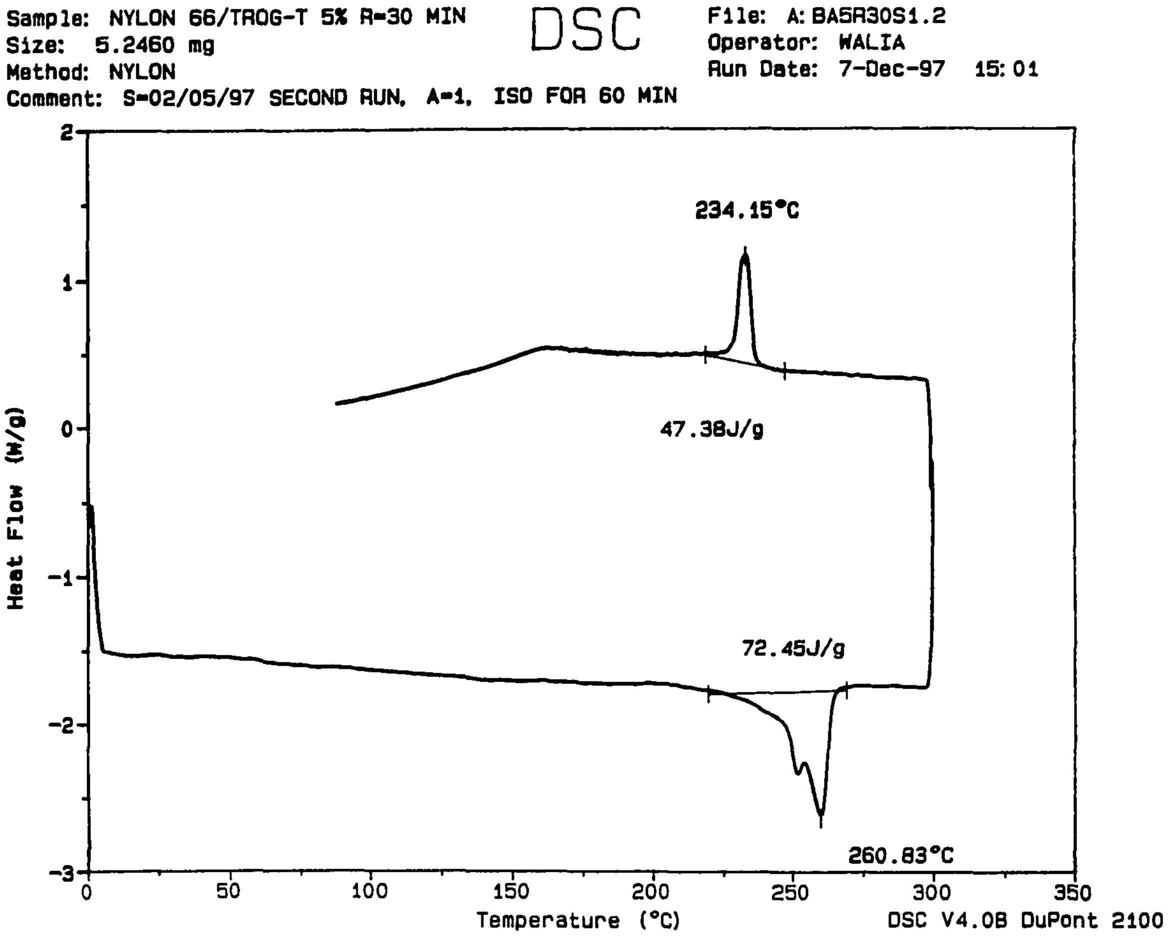


FIGURE B.22: DSC Run for 5% Nylon 6,6/Trogamid-T, RT=5 min Blend, Annealed for 1 hr (A=1)

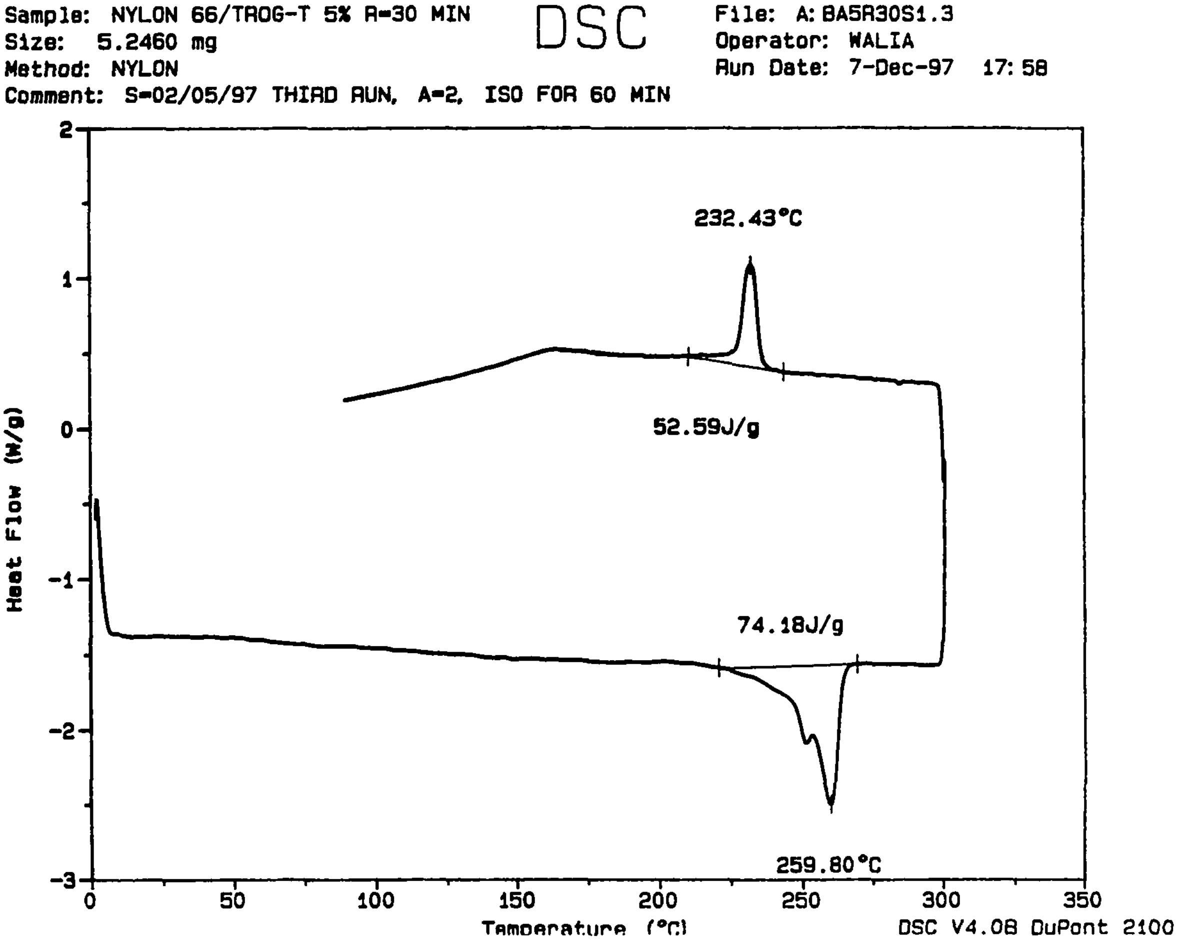


FIGURE B.23: DSC Run for 5% Nylon 6,6/Trogamid-T, RT=5 min Blend, Annealed for 2 hr (A=2)

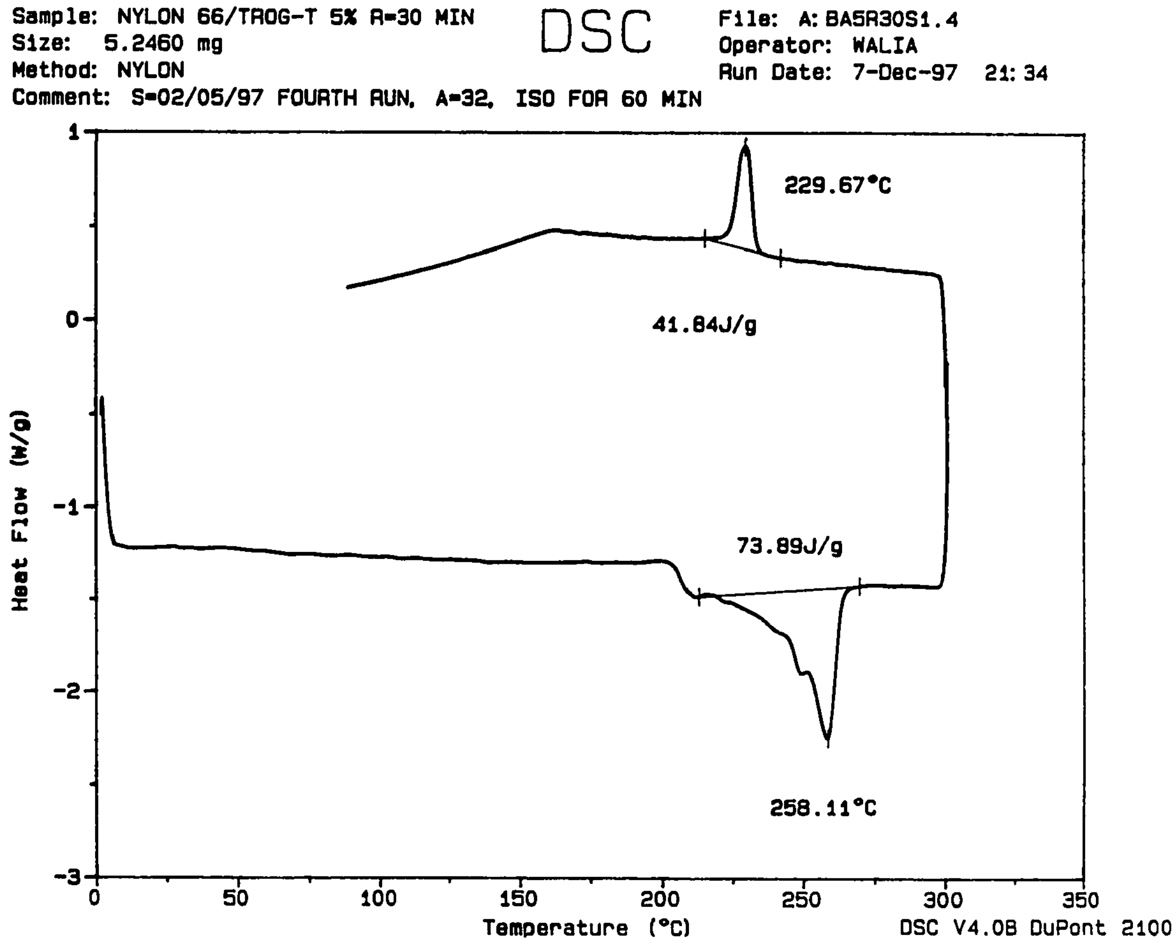


FIGURE B.24: DSC Run for 5% Nylon 6,6/Trogamid-T, RT=5 min Blend, Annealed for 3 hr (A=3)

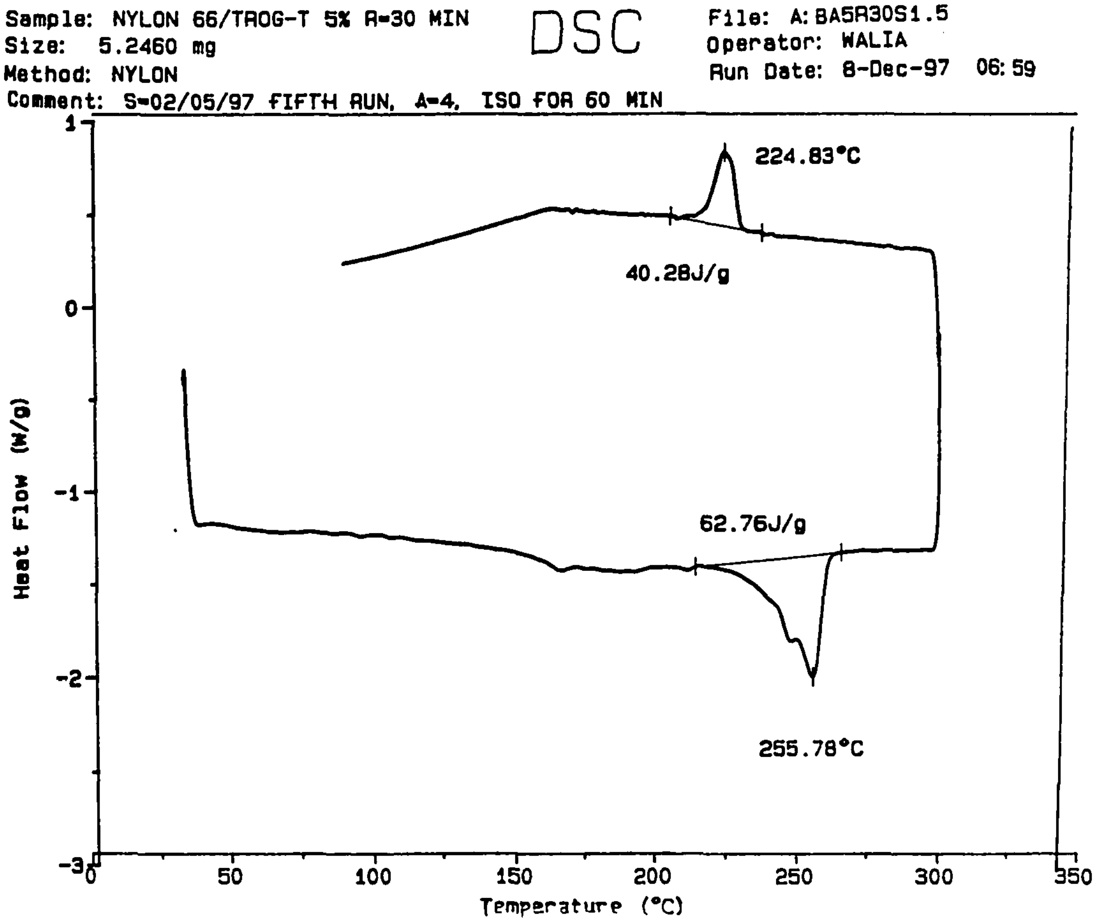
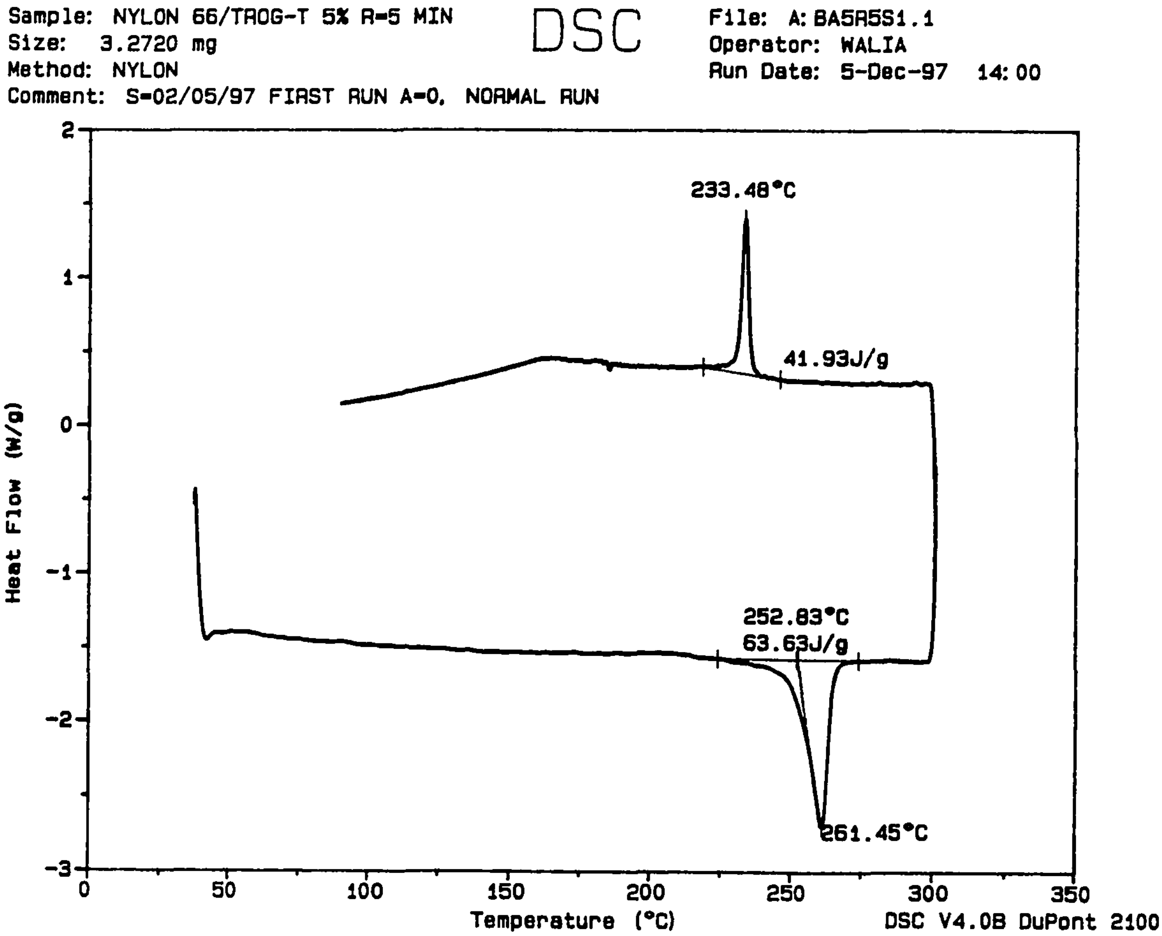


FIGURE B.25: DSC Run for 5% Nylon 6,6/Trogamid-T, RT=5 min Blend, Annealed for 4 hr (A=4)



Sample: NYLON 66/TROG-T 5% R=5 MIN
Size: 3.2720 mg
Method: NYLON
Comment: S=02/05/97 FIRST RUN A=0, NORMAL RUN

File: A: BA5R5S1.1
Operator: WALIA
Run Date: 5-Dec-97 14:00

FIGURE B.26: DSC Run for 5% Nylon 6,6/Trogamid-T, RT=30 min Blend, Unannealed (A=0)

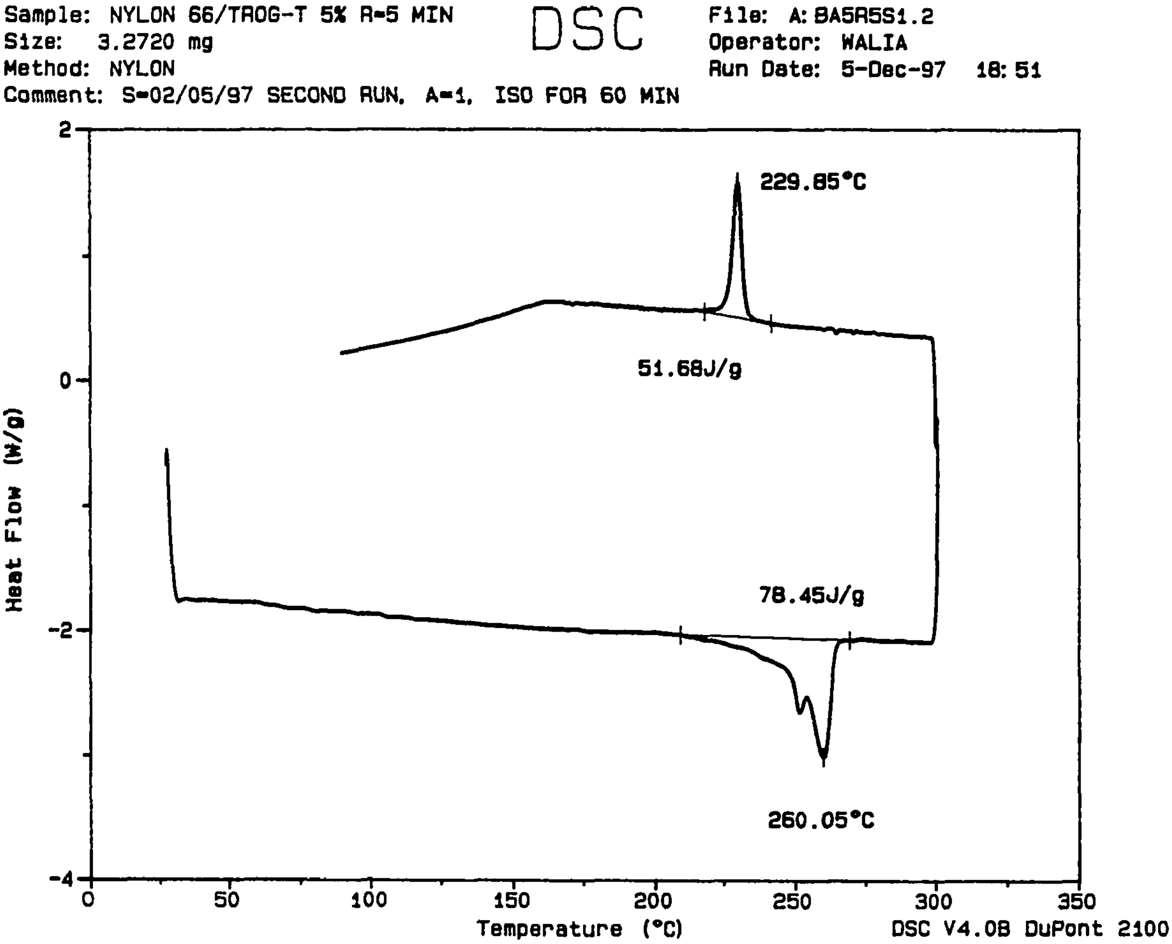


FIGURE B.27: DSC Run for 5% Nylon 6,6/Trogamid-T, RT=30 min Blend, Annealed for 1 hr (A=1)

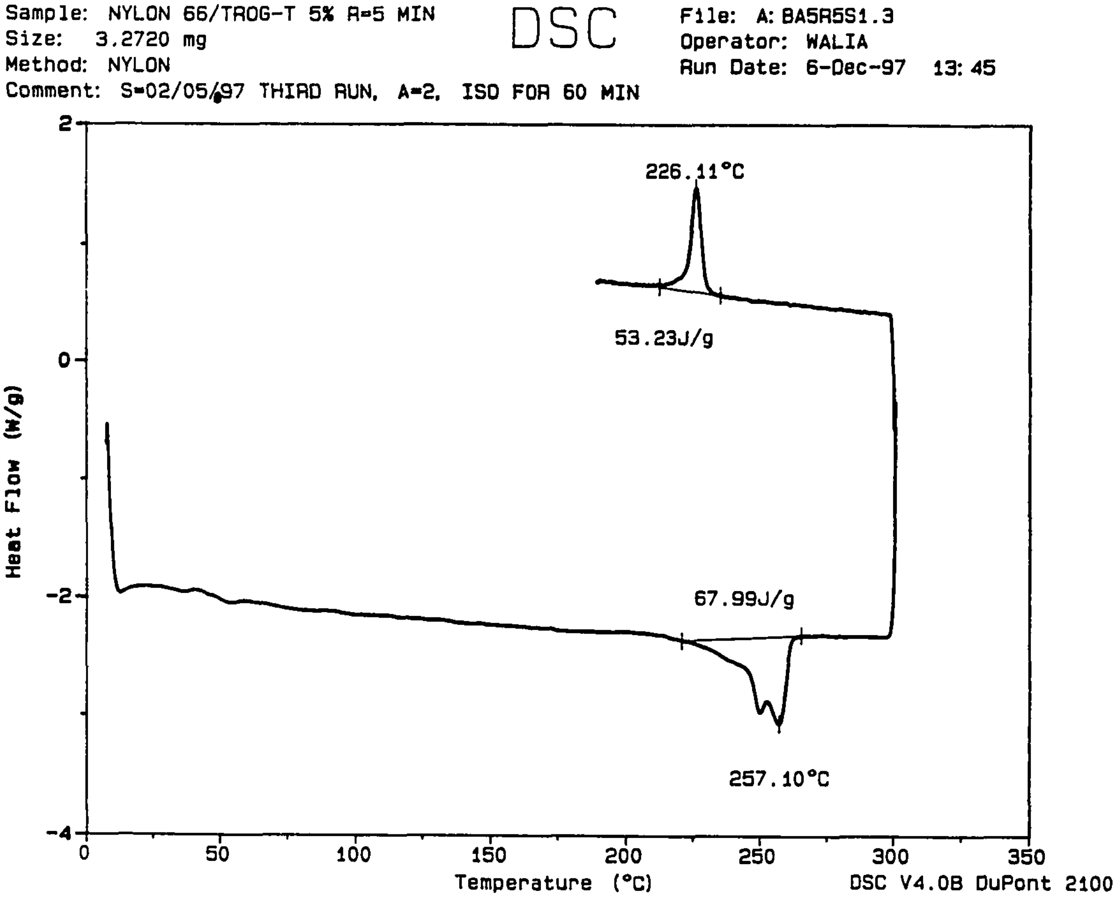


FIGURE B.28: DSC Run for 5% Nylon 6,6/Trogamid-T, RT=30 min Blend, Annealed for 2 hr (A=2)

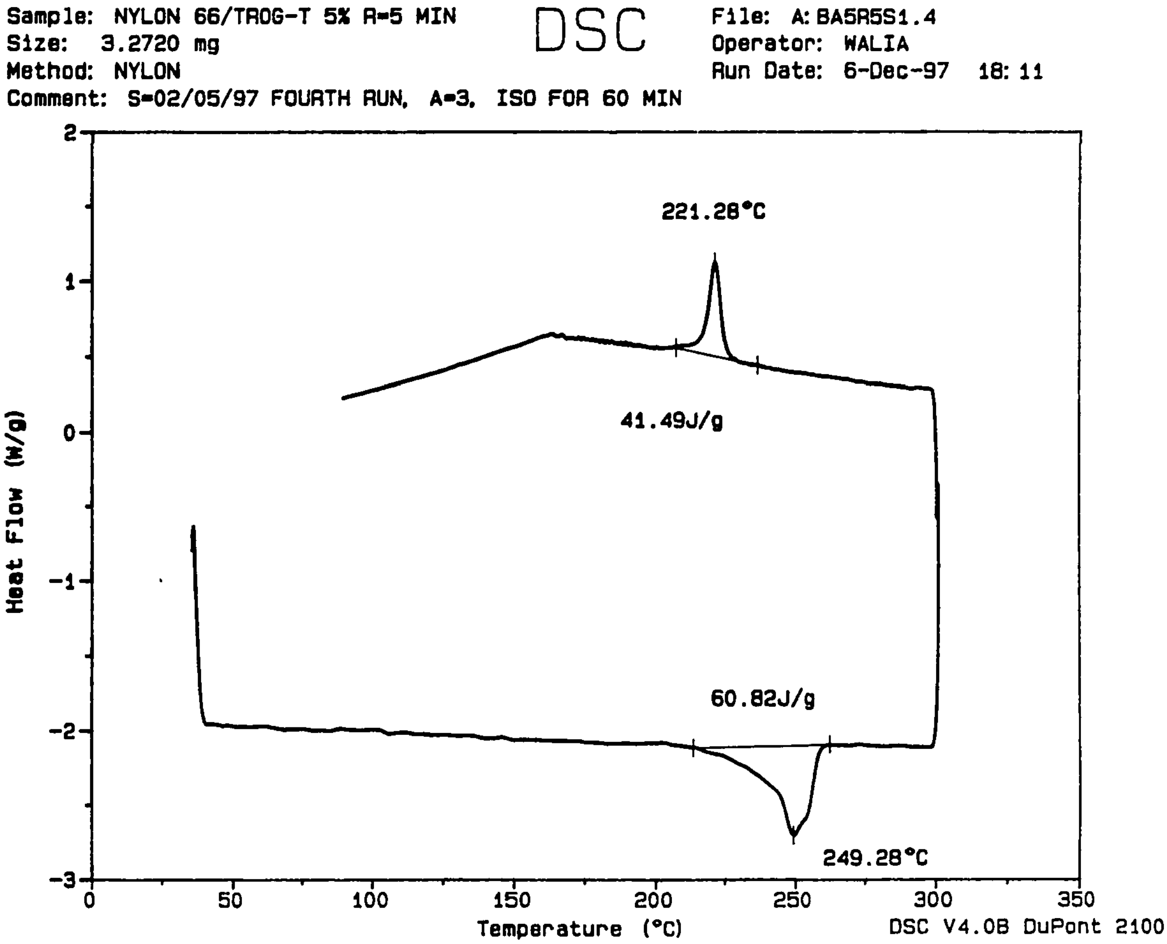


FIGURE B.29: DSC Run for 5% Nylon 6,6/Trogamid-T, RT=30 min Blend, Annealed for 3 hr (A=3)

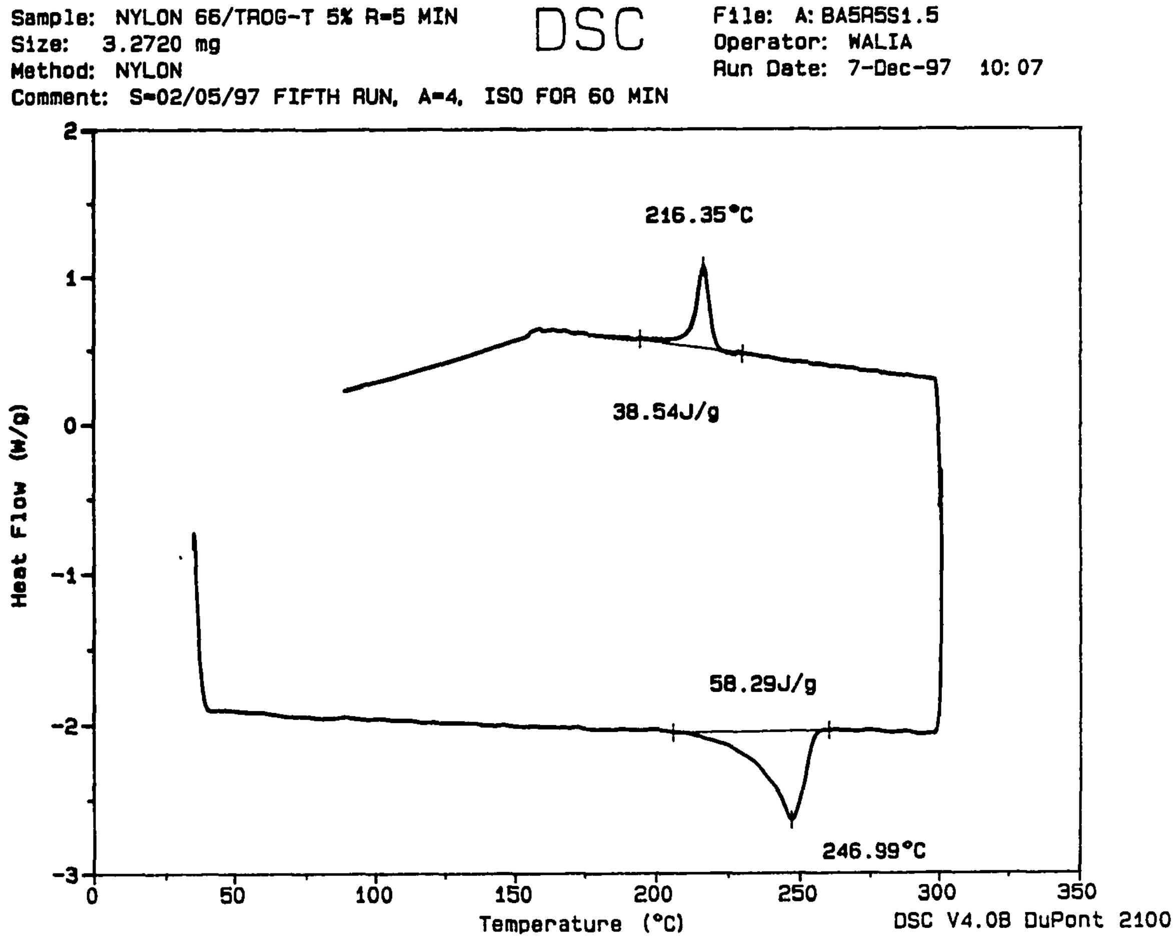


FIGURE B.30: DSC Run for 5% Nylon 6,6/Trogamid-T, RT=30 min Blend, Annealed for 4 hr (A=4)

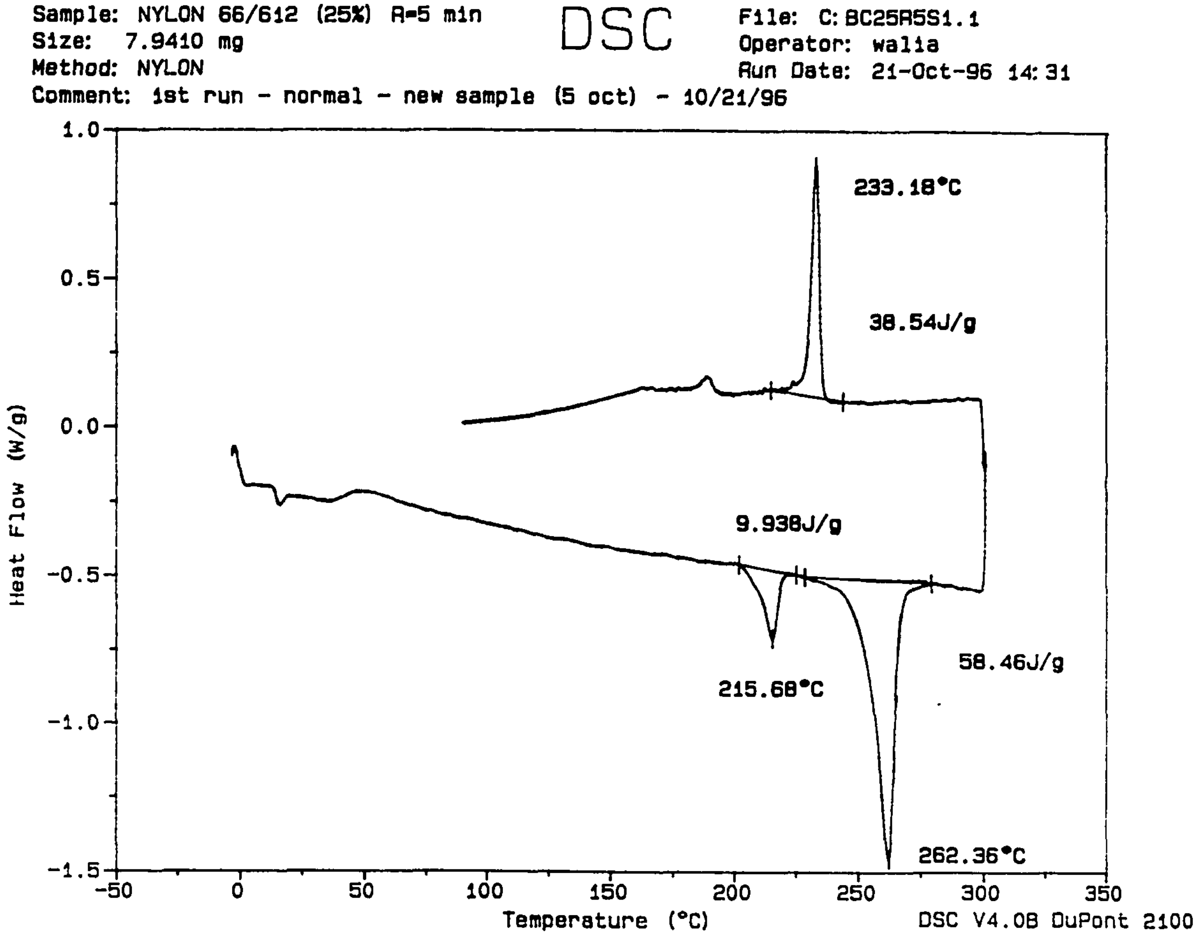


FIGURE B.31: DSC Run for 25% Nylon 6,6/Nylon 6,12, RT=5 min Blend, Unannealed (A=0)

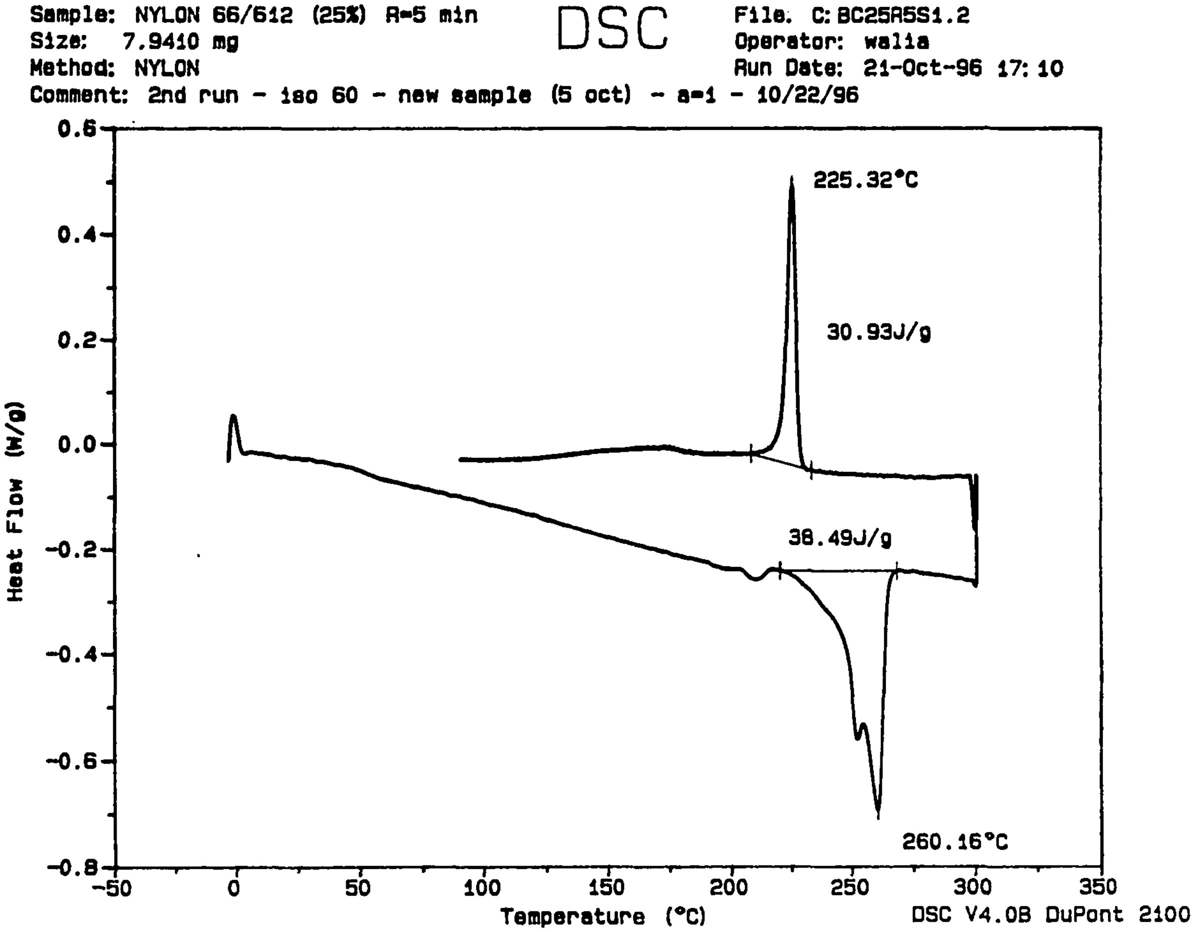
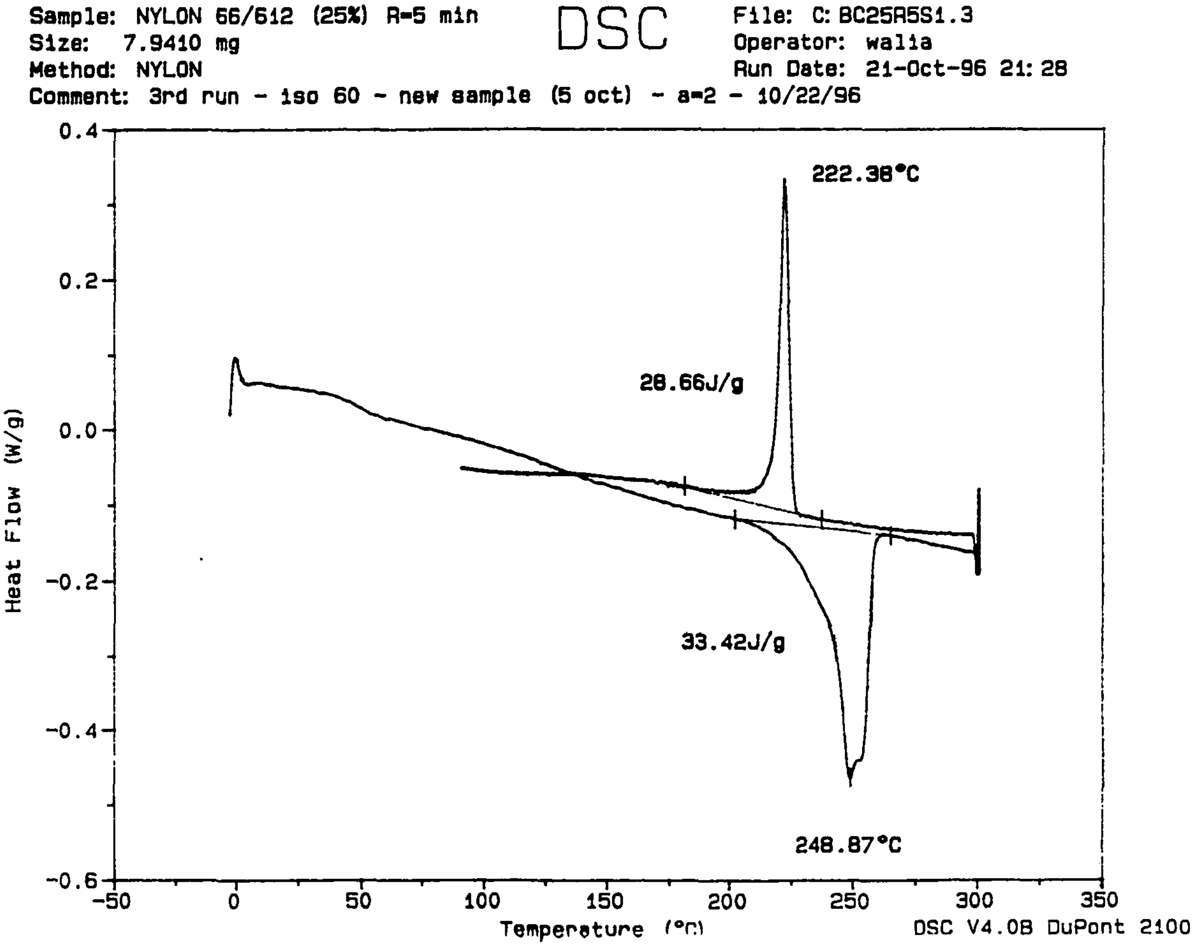


FIGURE B.32: DSC Run for 25% Nylon 6,6/Nylon 6,12, RT=5 min Blend, Annealed for 1 hr (A=1)



Sample: NYLON 66/612 (25%) R=5 min
Size: 7.9410 mg
Method: NYLON
Comment: 3rd run - iso 60 - new sample (5 oct) - a=2 - 10/22/96

DSC

File: C:BC25R5S1.3
Operator: walia
Run Date: 21-Oct-96 21:28

FIGURE B.33: DSC Run for 25% Nylon 6,6/Nylon 6,12, RT=5 min Blend, Annealed for 2 hrs (A=2)

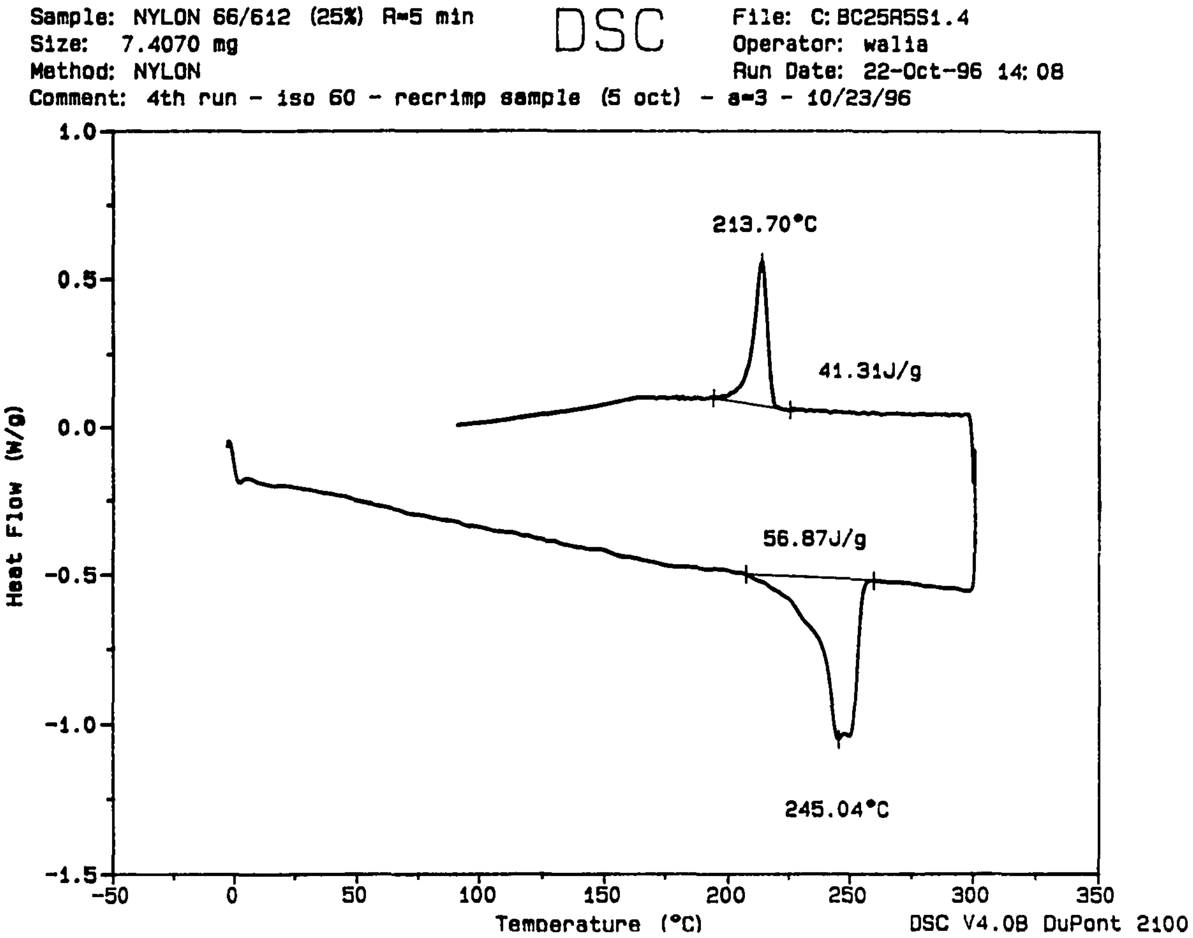


FIGURE B.34: DSC Run for 25% Nylon 6,6/Nylon 6,12, RT=5 min Blend, Annealed for 3 hrs (A=3)

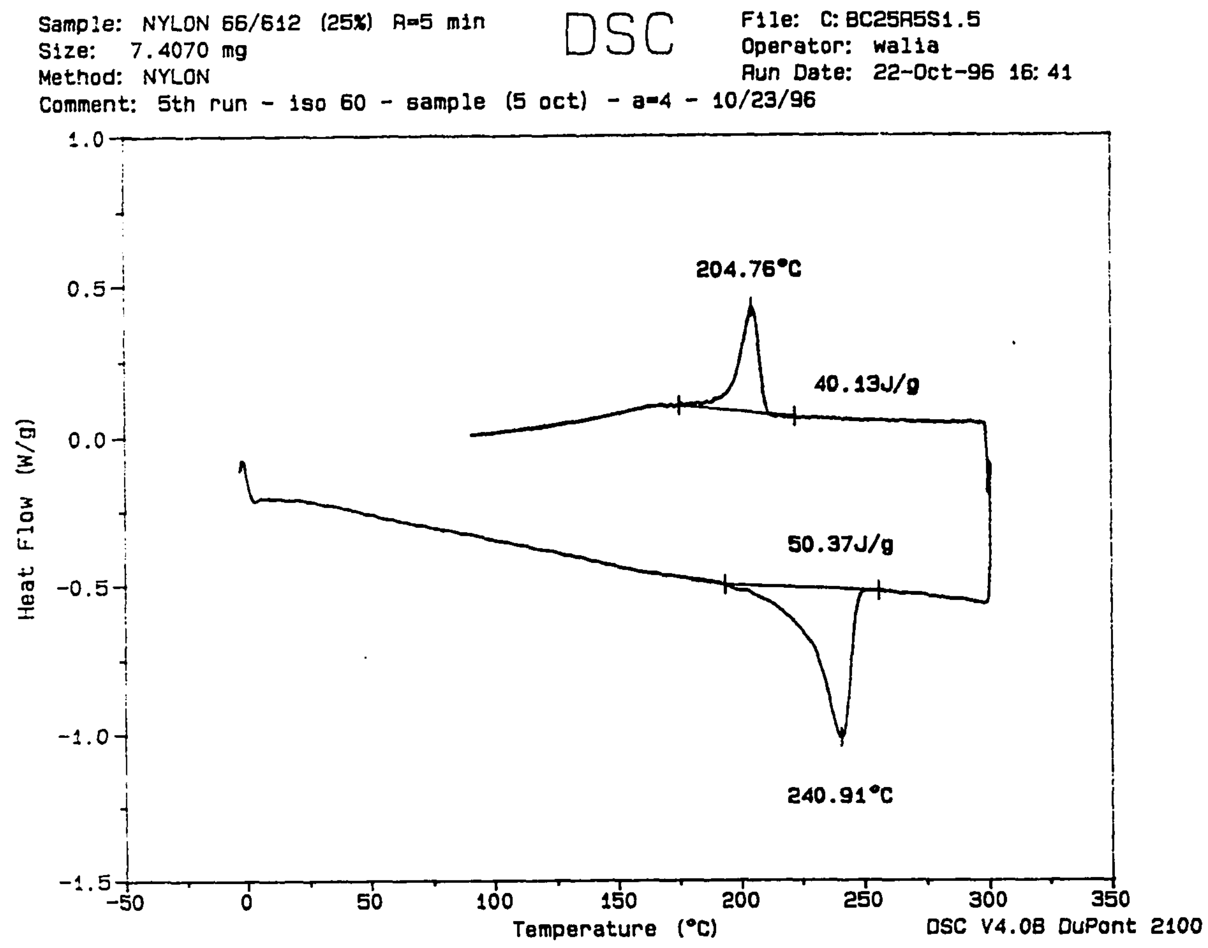


FIGURE B.35: DSC Run for 25% Nylon 6,6/Nylon 6,12, RT=5 min Blend, Annealed for 4 hrs (A=4)

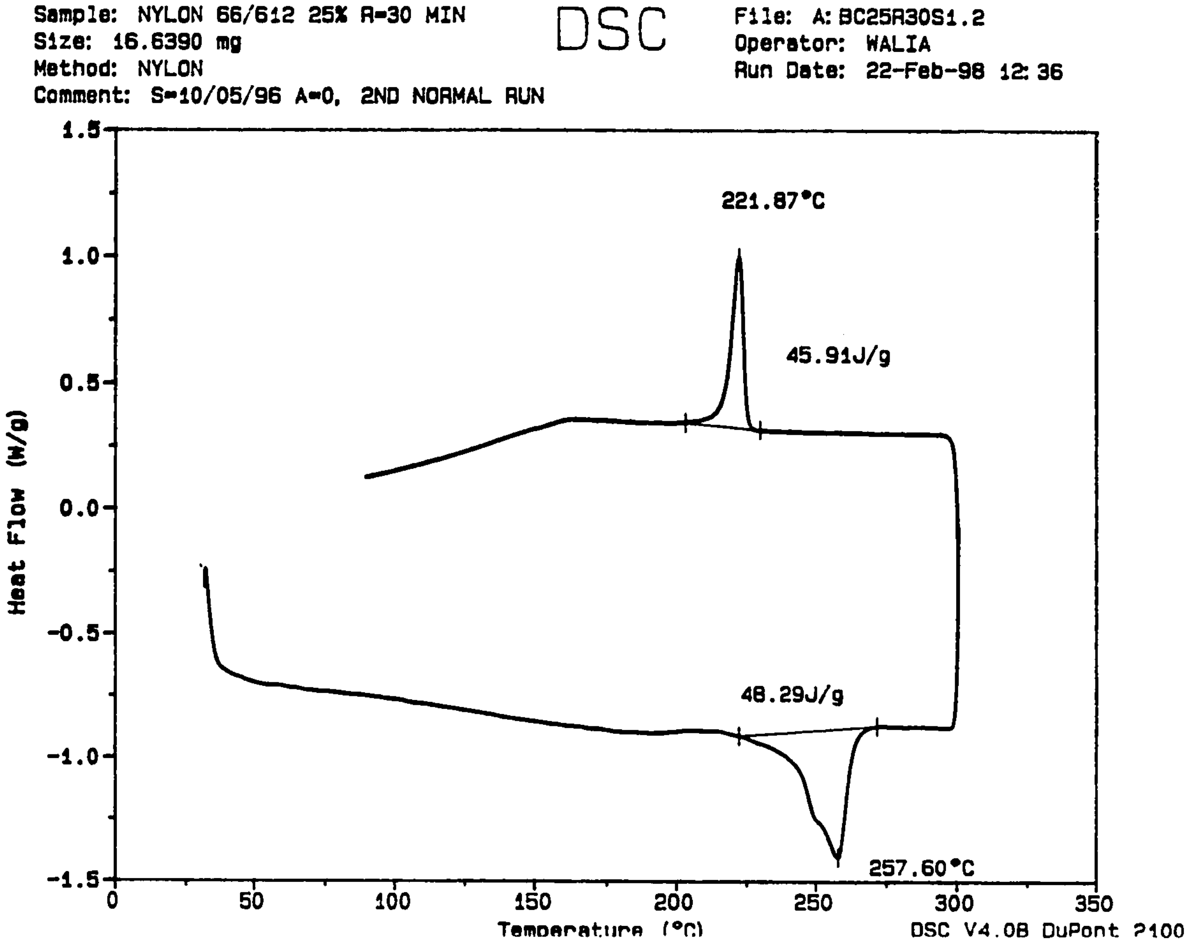


FIGURE B.36: DSC Run for 25% Nylon 6,6/Nylon 6,12, RT=30 min Blend, Unannealed (A=0)

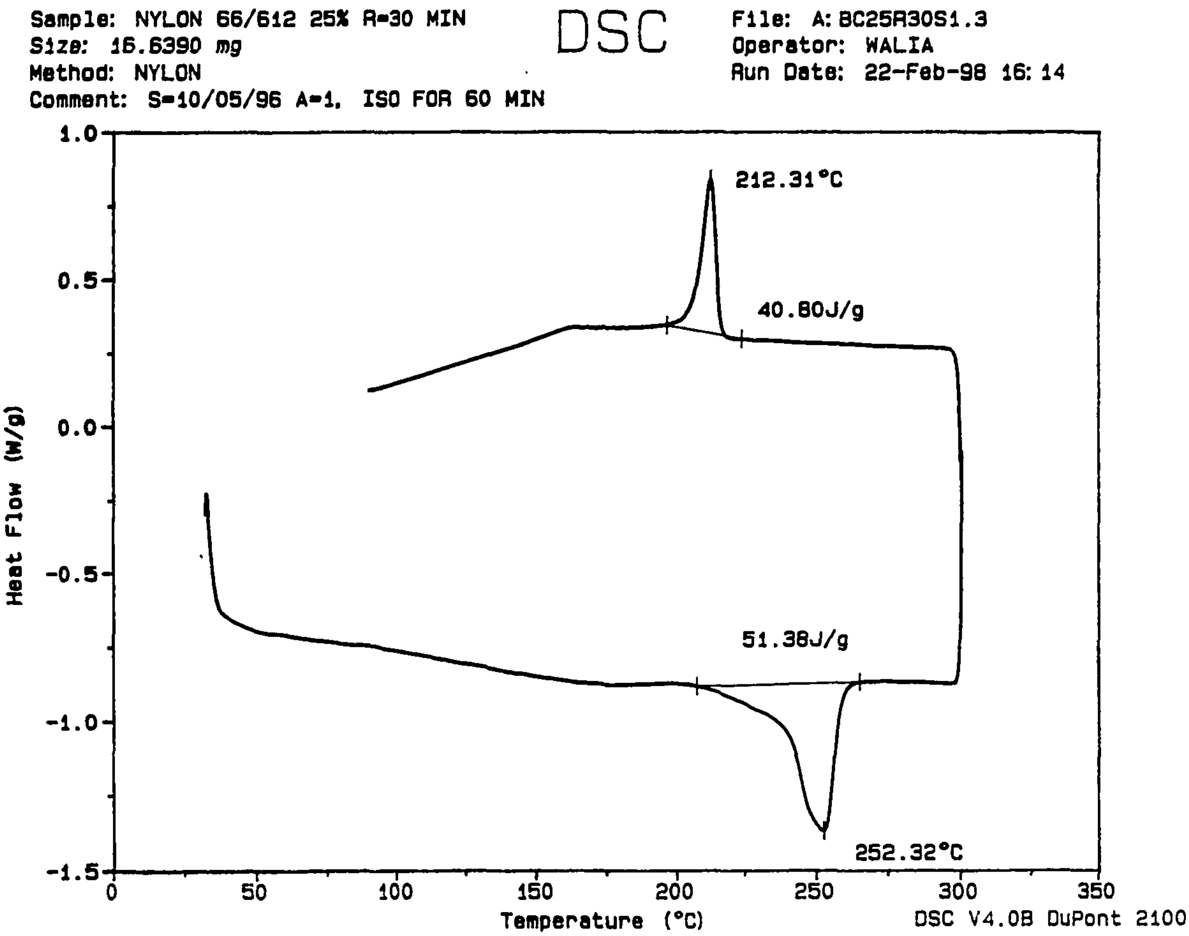


FIGURE B.37: DSC Run for 25% Nylon 6,6/Nylon 6,12, RT=30 min Blend, Annealed for 1 hr (A=1)

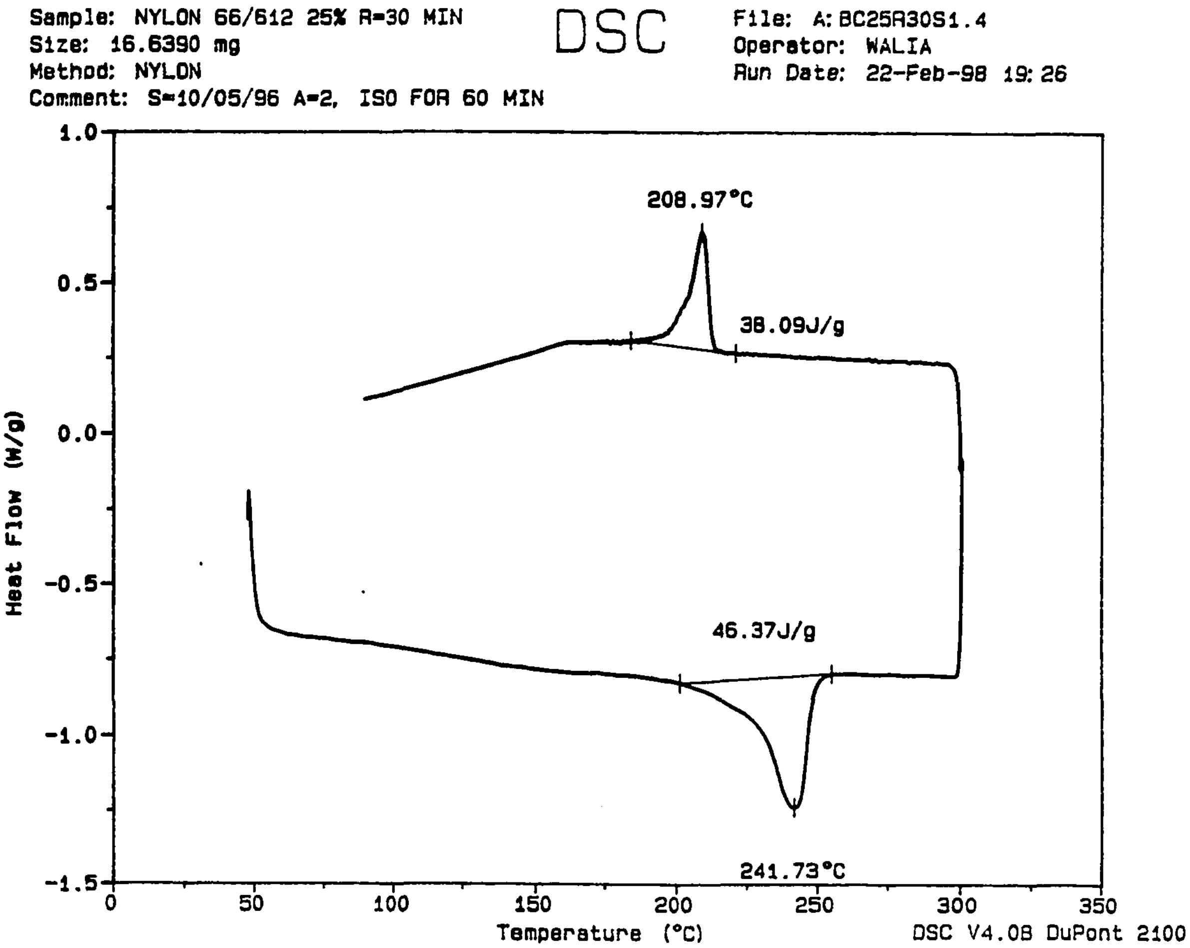


FIGURE B.38: DSC Run for 25% Nylon 6,6/Nylon 6,12, RT=30 min Blend, Annealed for 2 hrs (A=2)

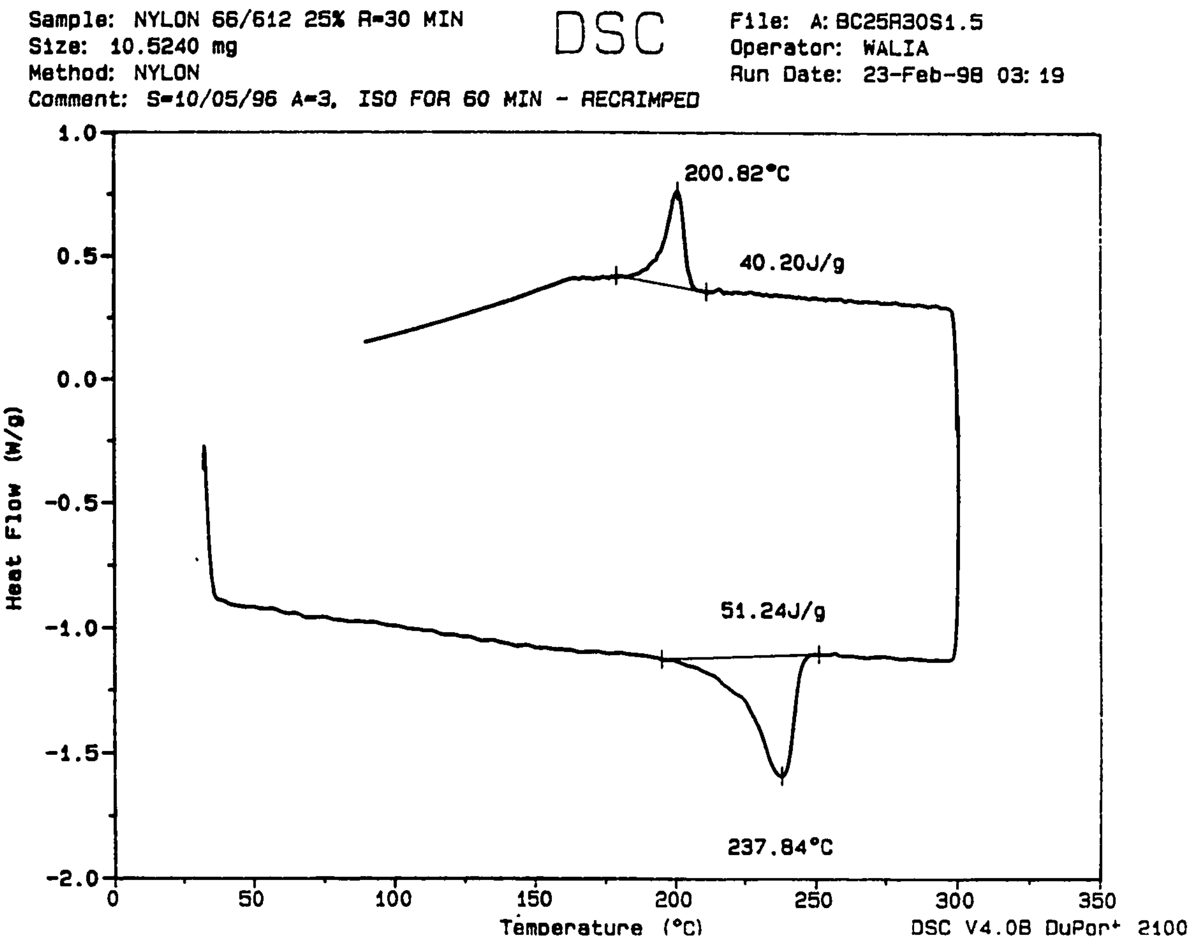


FIGURE B.39: DSC Run for 25% Nylon 6,6/Nylon 6,12, RT=30 min Blend, Annealed for 3 hrs (A=3)

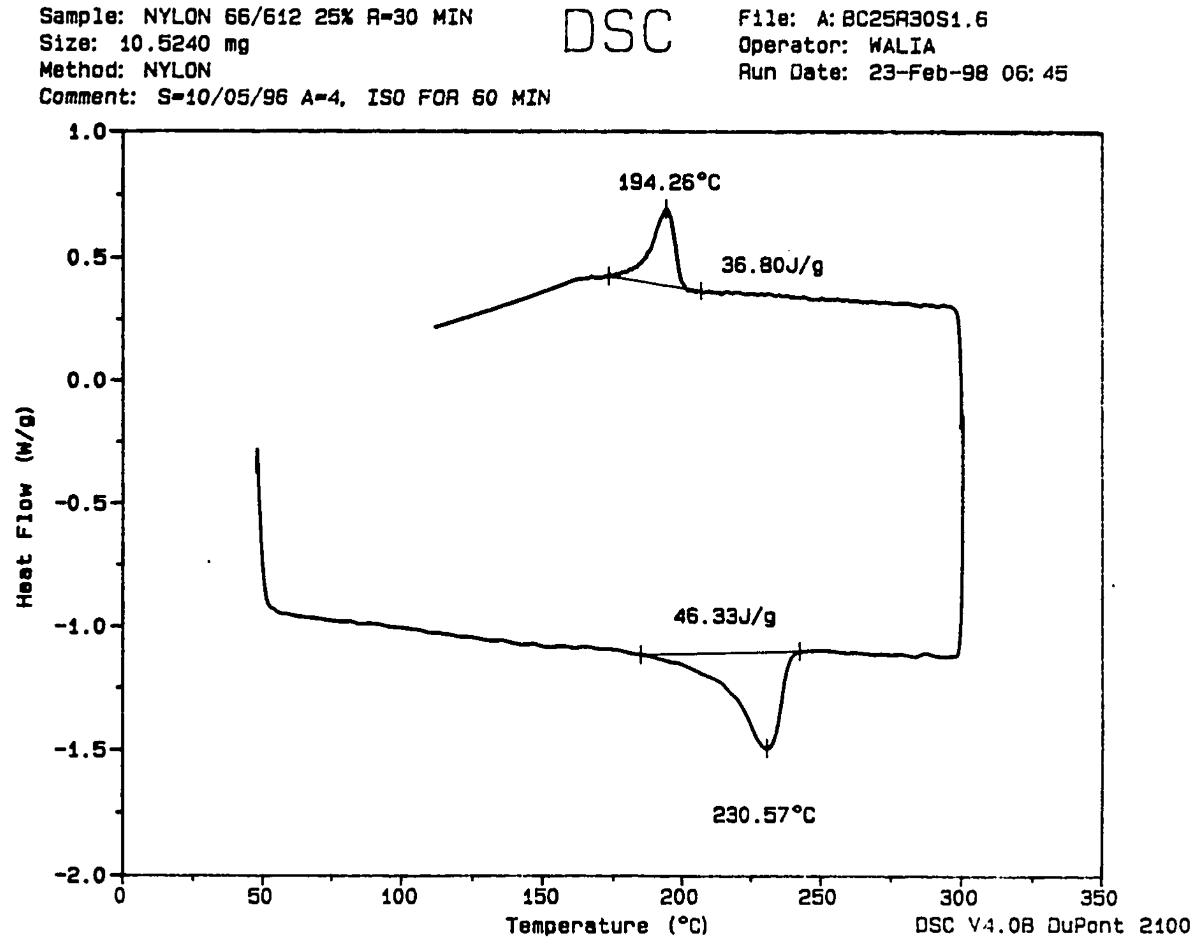


FIGURE B.40: DSC Run for 25% Nylon 6,6/Nylon 6,12, RT=30 min Blend, Annealed for 4 hrs (A=4)

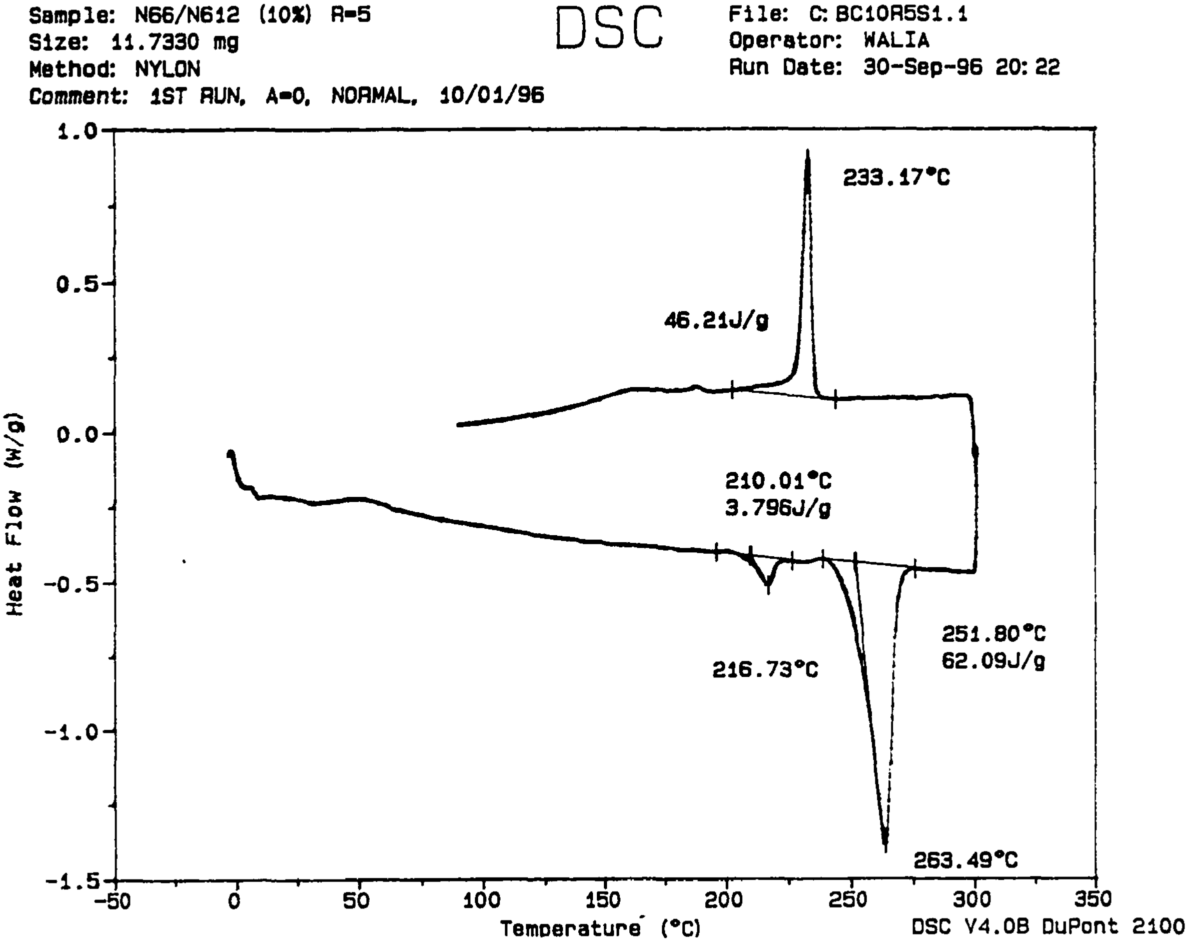


FIGURE B.41: DSC Run for 10% Nylon 6,6/Nylon 6,12, RT=5 min Blend, Unannealed (A=0)

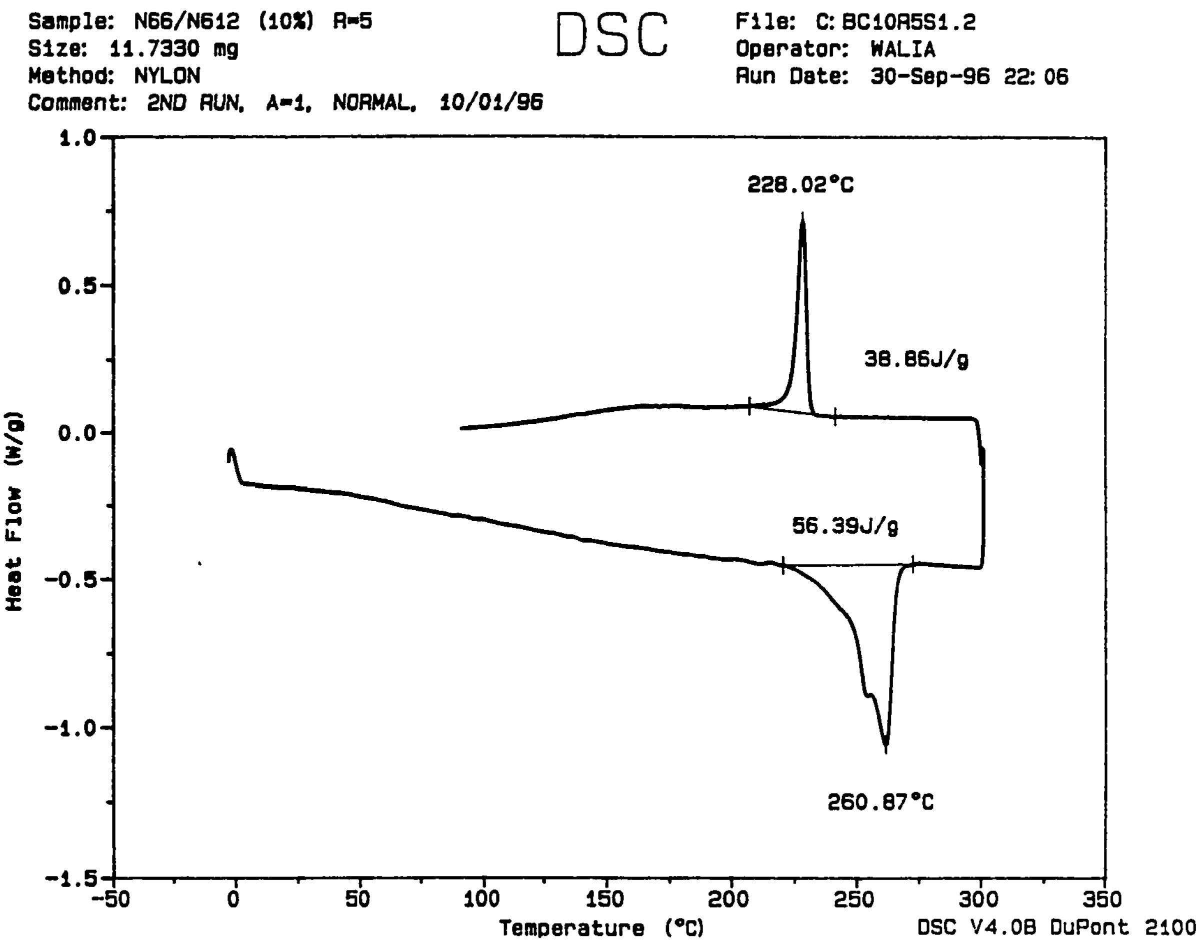


FIGURE B.42: DSC Run for 10% Nylon 6,6/Nylon 6,12, RT=5 min Blend, Annealed for 1 hr (A=1)

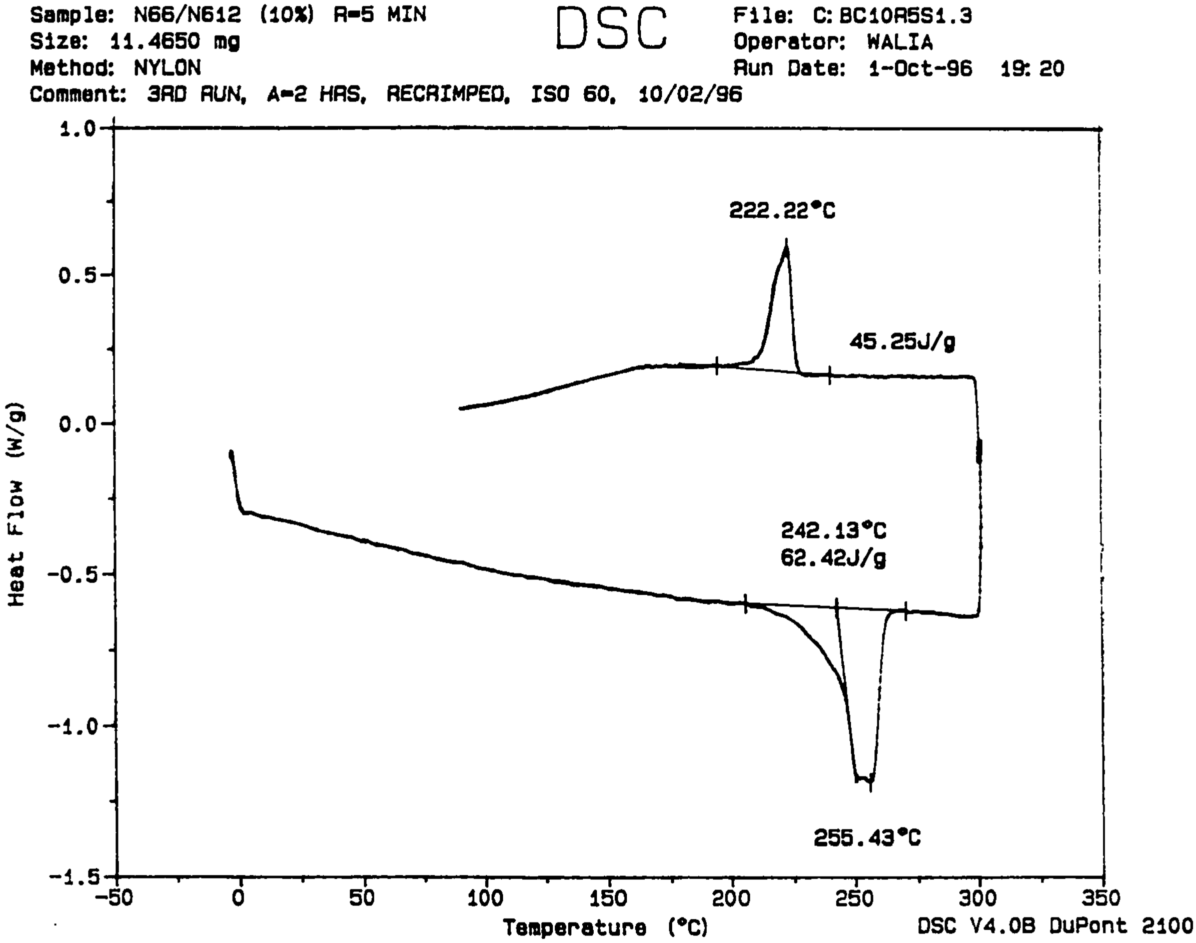


FIGURE B.43: DSC Run for 10% Nylon 6,6/Nylon 6,12, RT=5 min Blend, Annealed for 2 hr (A=2)

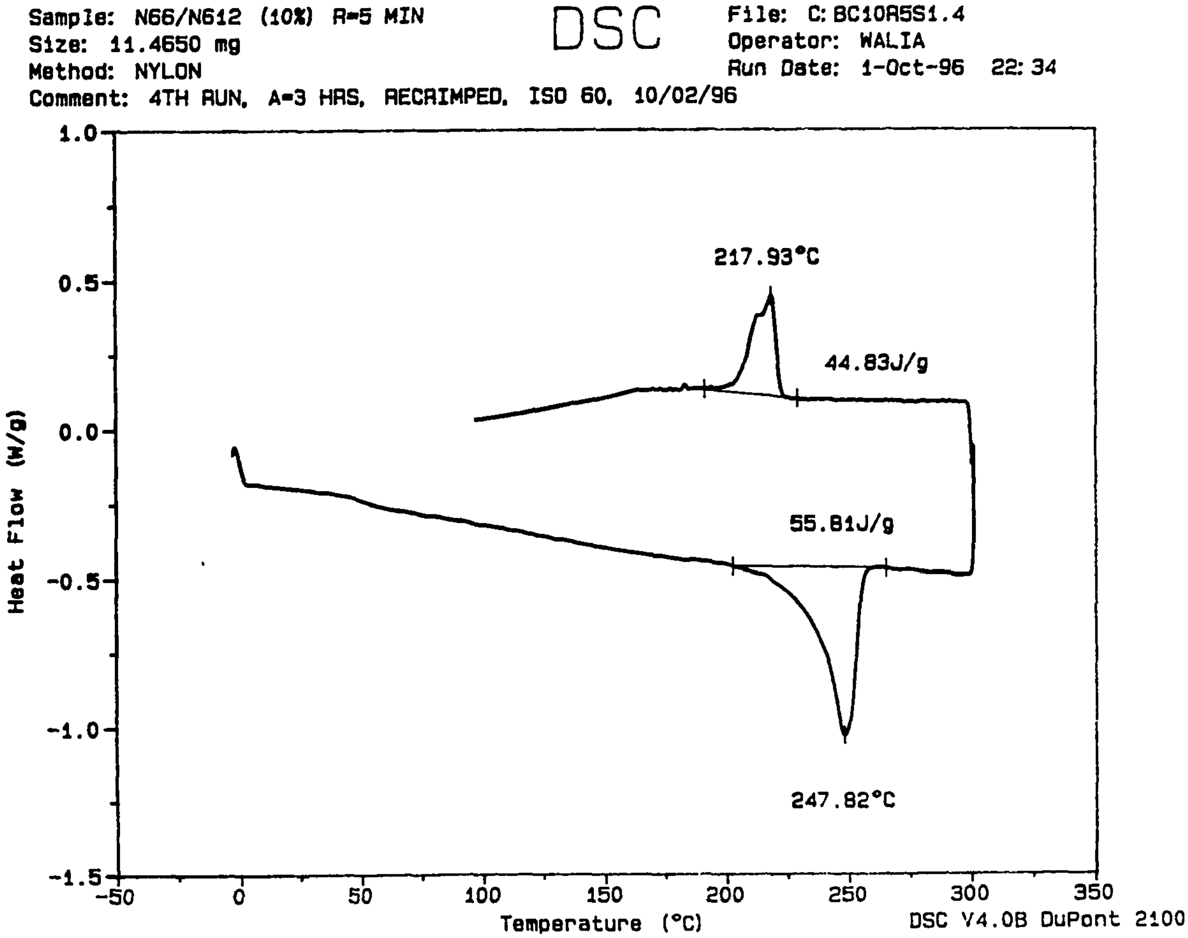


FIGURE B.44: DSC Run for 10% Nylon 6,6/Nylon 6,12, RT=5 min Blend, Annealed for 3 hr (A=3)

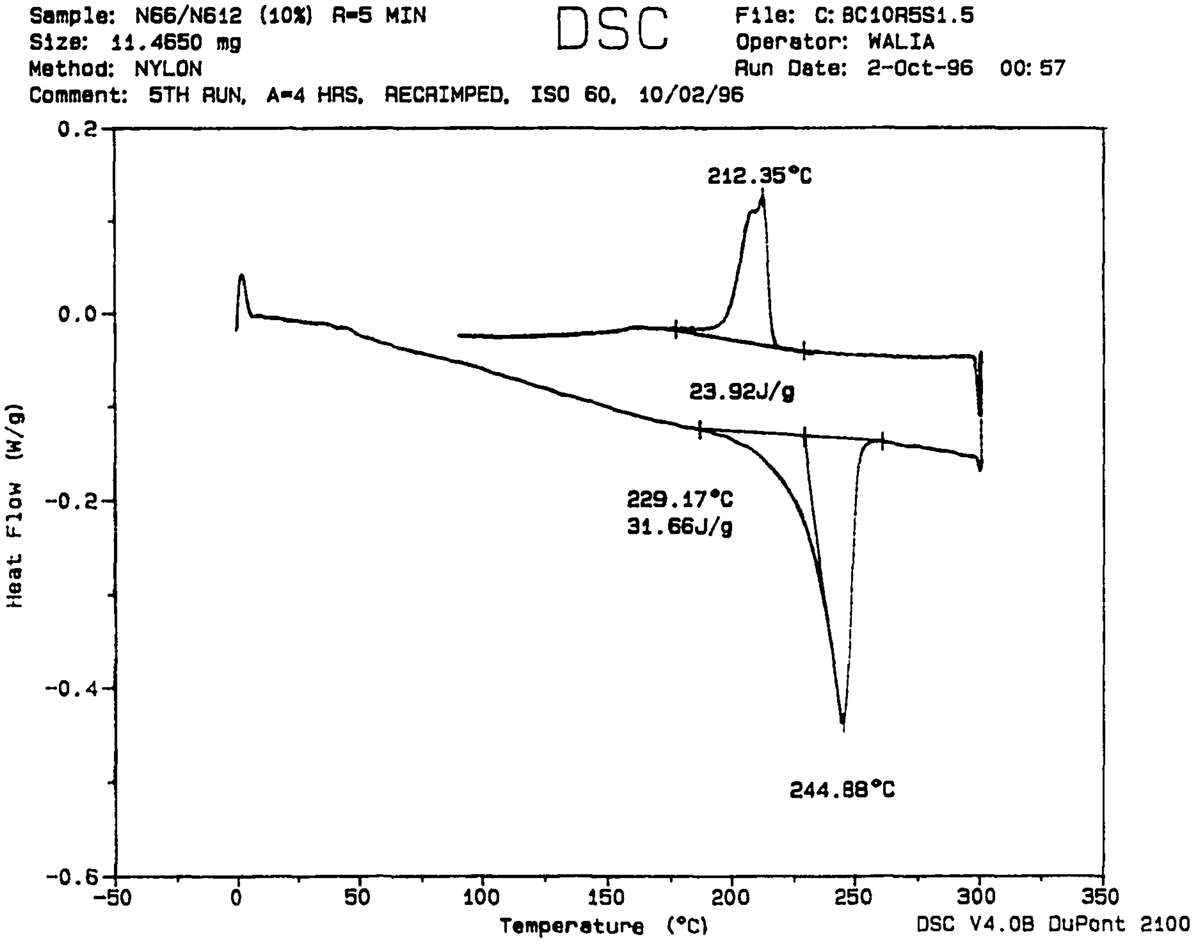
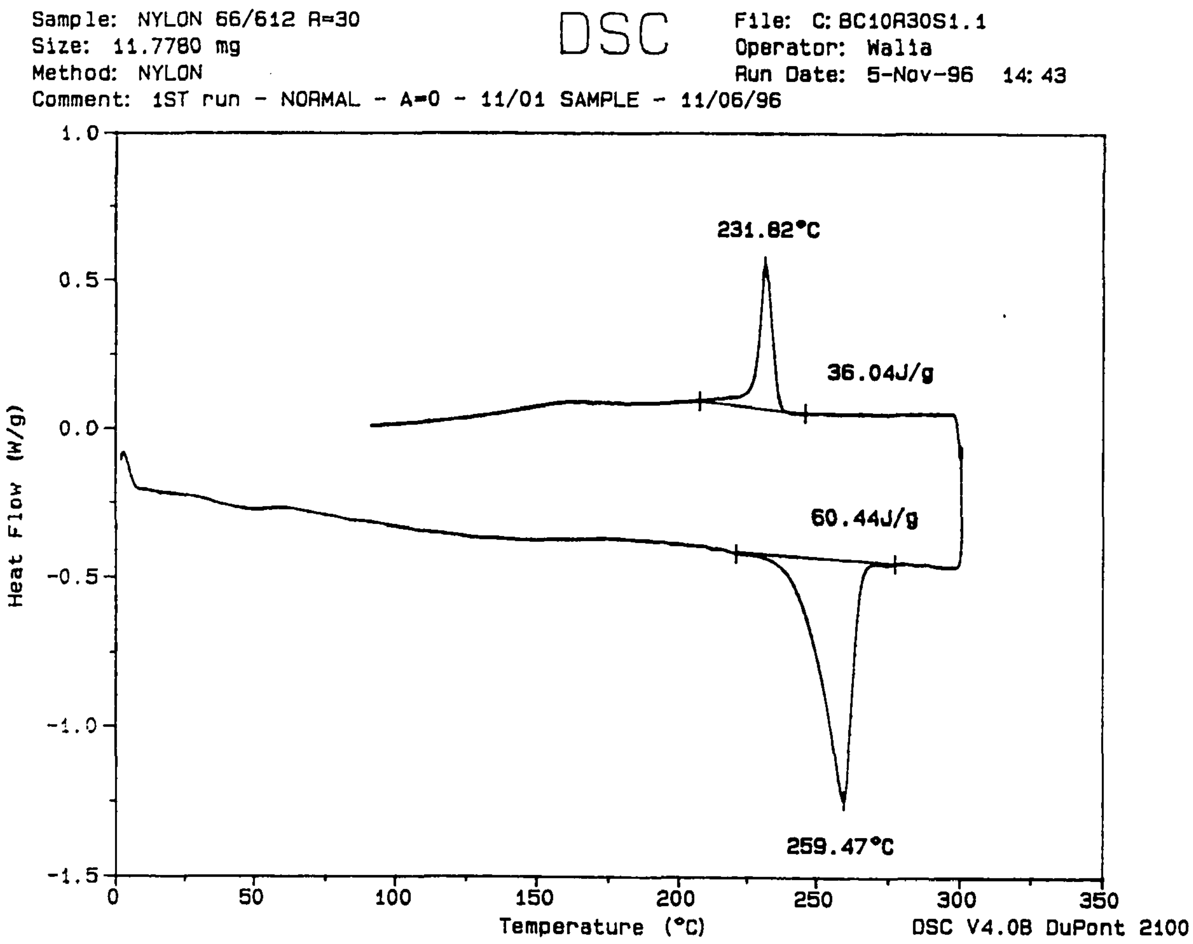


FIGURE B.45: DSC Run for 10% Nylon 6,6/Nylon 6,12, RT=5 min Blend, Annealed for 4 hr (A=4)



Sample: NYLON 66/612 R=30
Size: 11.7780 mg
Method: NYLON
Comment: 1ST run - NORMAL - A=0 - 11/01 SAMPLE - 11/06/96

DSC

File: C:BC10R30S1.1
Operator: Walia
Run Date: 5-Nov-96 14:43

FIGURE B.46: DSC Run for 10% Nylon 6,6/Nylon 6,12, RT=30 min Blend, Unannealed (A=0)

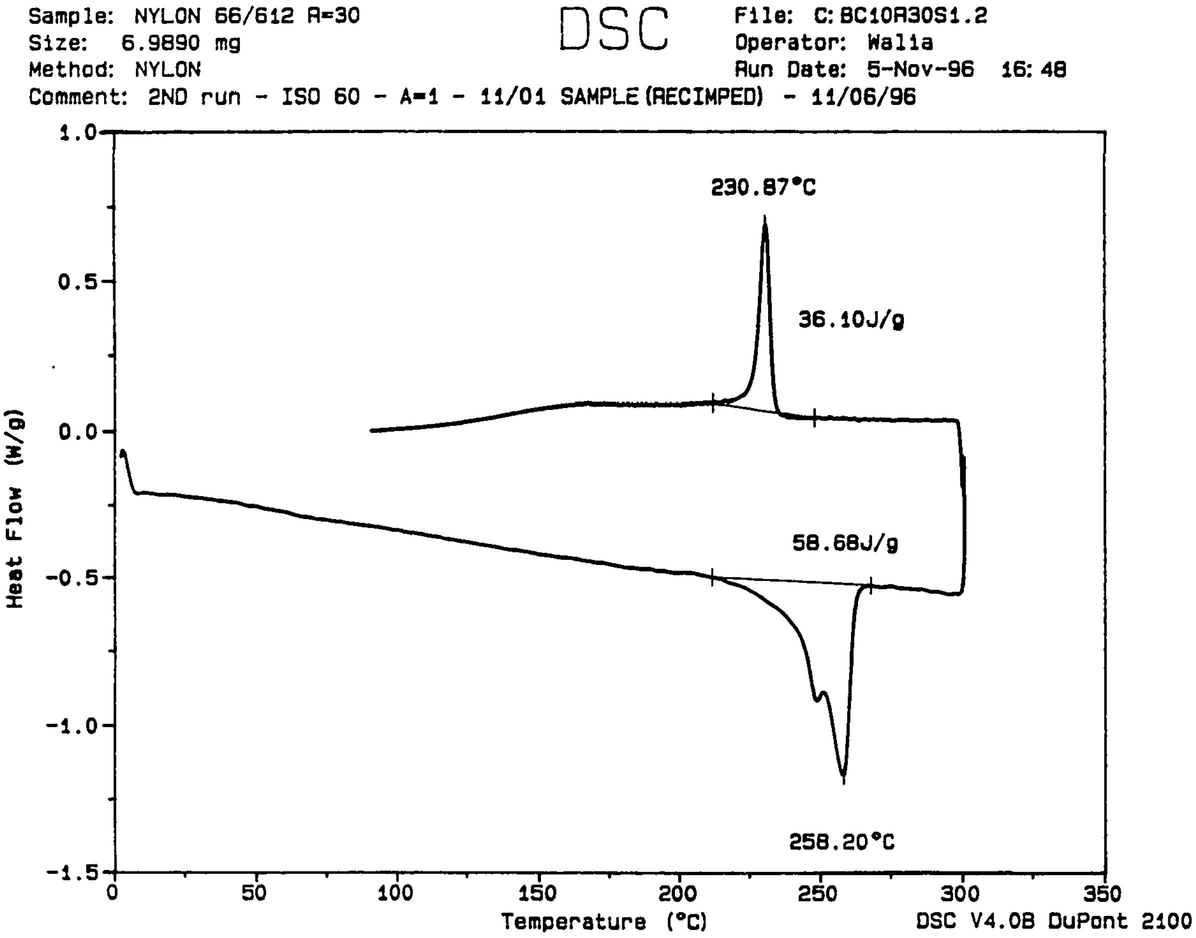


FIGURE B.47: DSC Run for 10% Nylon 6,6/Nylon 6,12, RT=30 min Blend, Annealed for 1 hr (A=1)

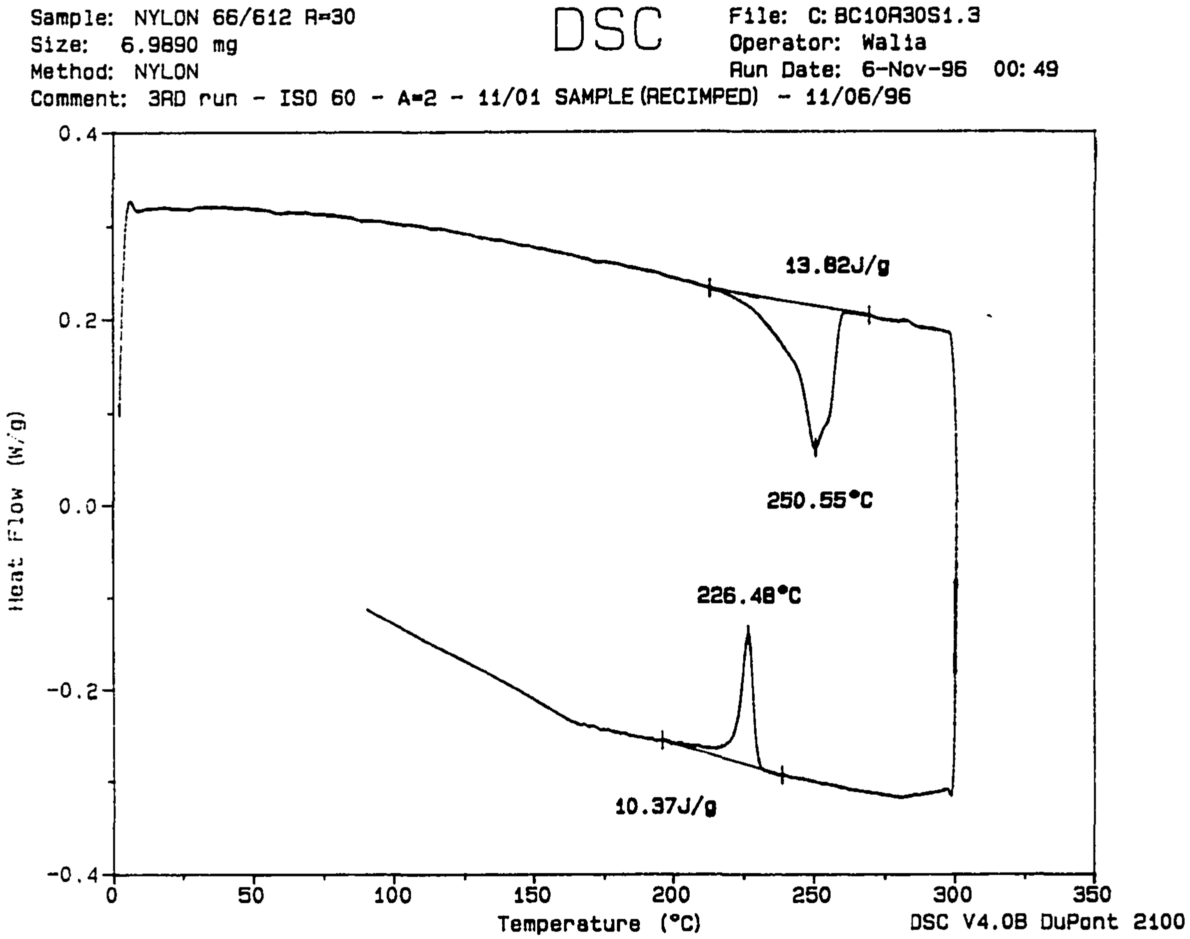


FIGURE B.48: DSC Run for 10% Nylon 6,6/Nylon 6,12, RT=30 min Blend, Annealed for 2 hr (A=2)

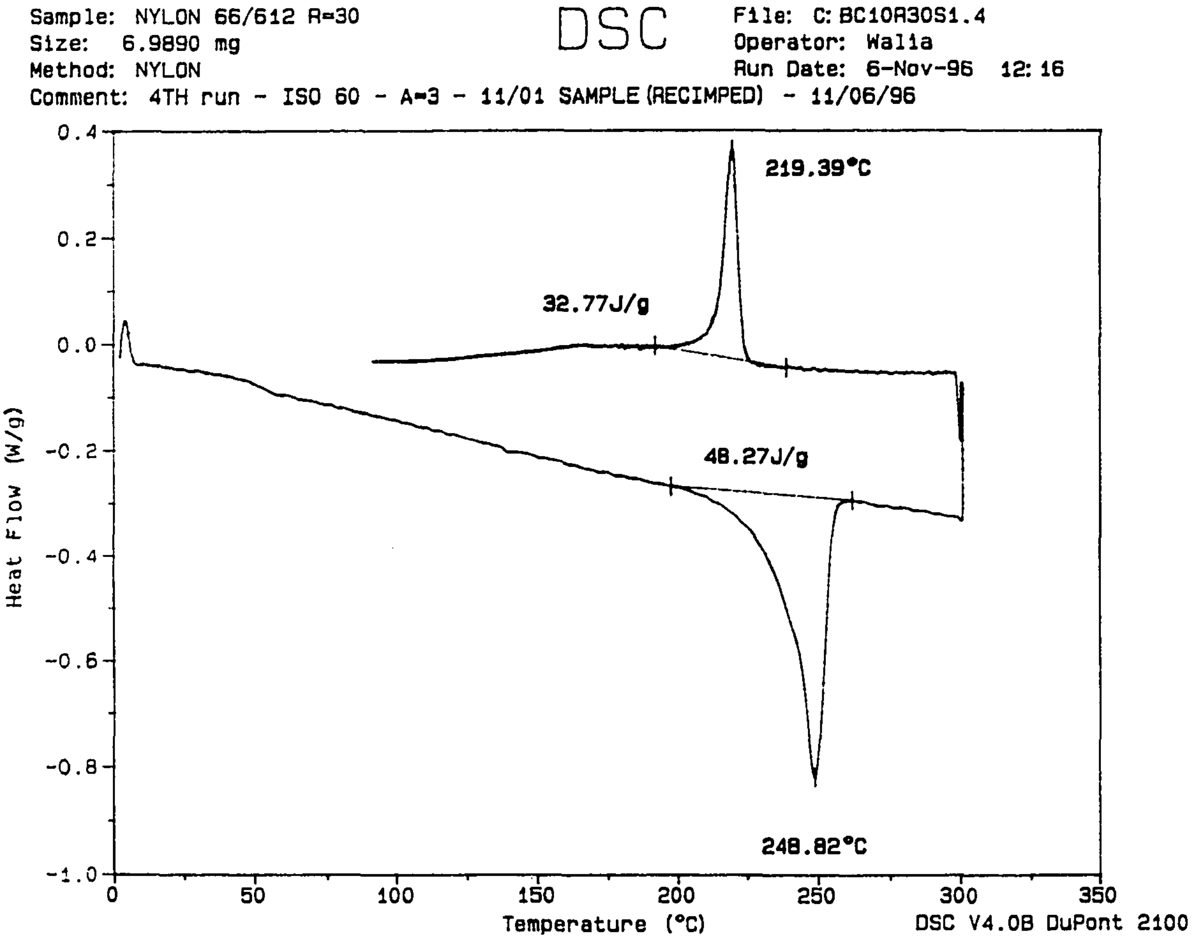


FIGURE B.49: DSC Run for 10% Nylon 6,6/Nylon 6,12, RT=30 min Blend, Annealed for 3 hr (A=3)

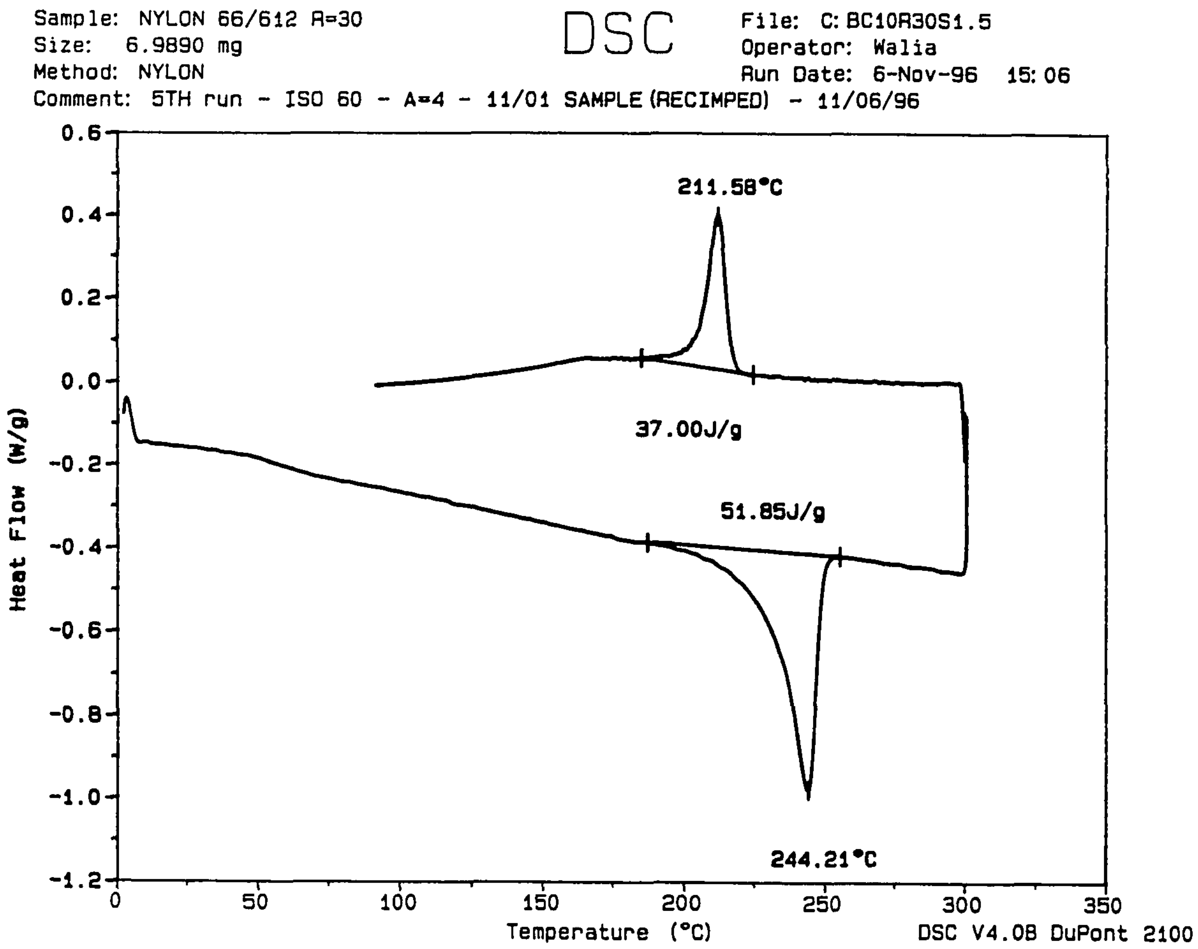


FIGURE B.50: DSC Run for 10% Nylon 6,6/Nylon 6,12, RT=30 min Blend, Annealed for 4 hr (A=4)

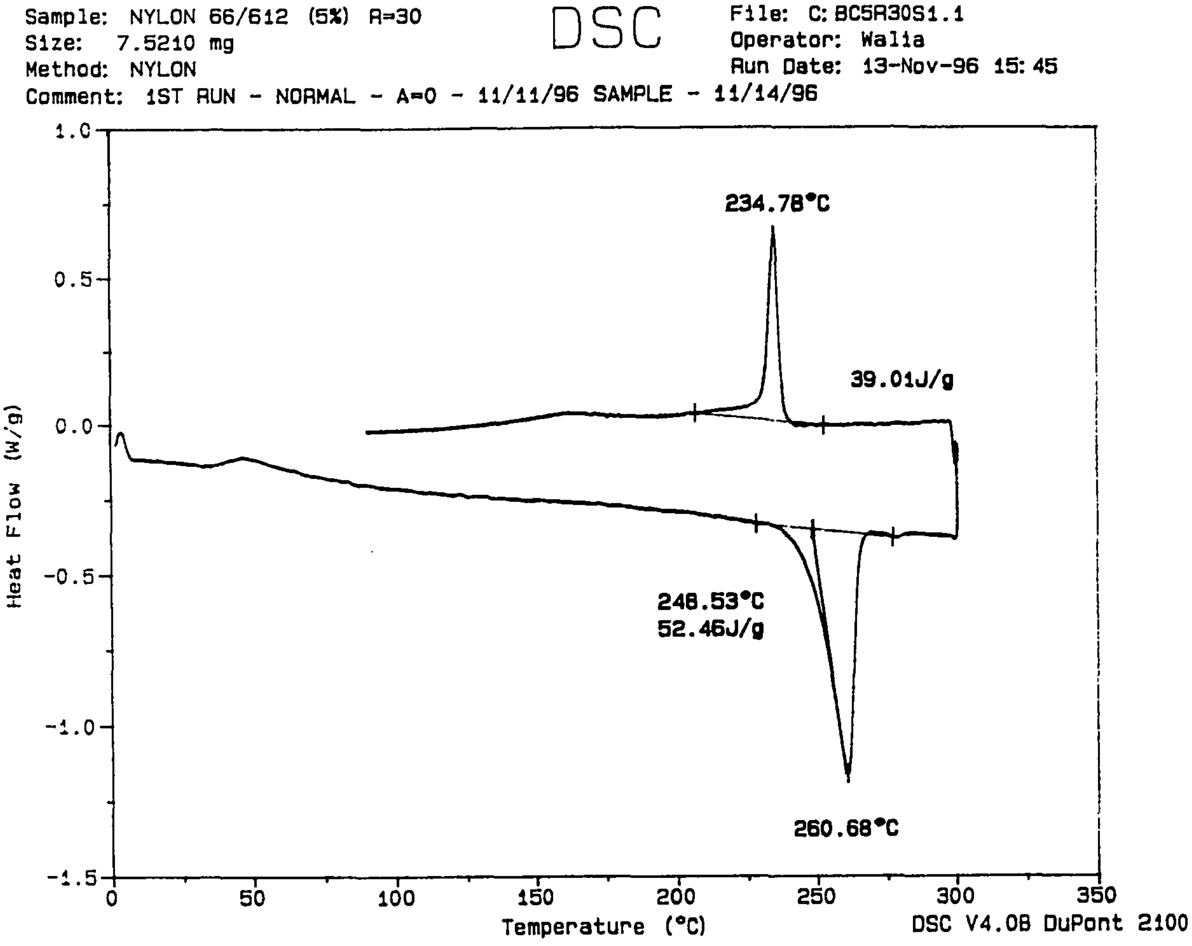
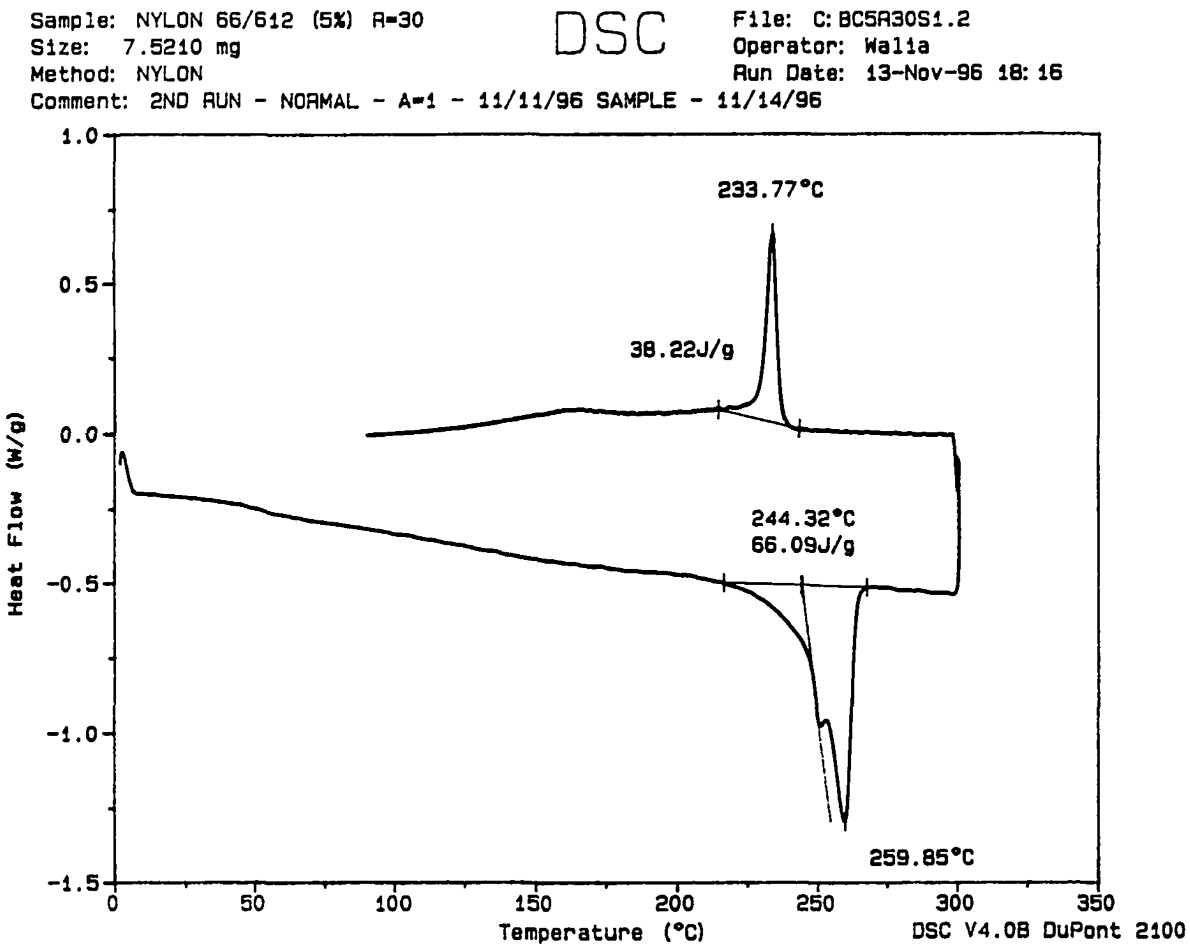


FIGURE B.51: DSC Run for 5% Nylon 6,6/Nylon 6,12, RT=5 min Blend, Unannealed (A=0)



Sample: NYLON 66/612 (5%) R=30
Size: 7.5210 mg
Method: NYLON
Comment: 2ND RUN - NORMAL - A=1 - 11/11/96 SAMPLE - 11/14/96

File: C:BC5R30S1.2
Operator: Walia
Run Date: 13-Nov-96 18:16

FIGURE B.52: DSC Run for 5% Nylon 6,6/Nylon 6,12, RT=5 min Blend, Annealed for 1 hr (A=1)

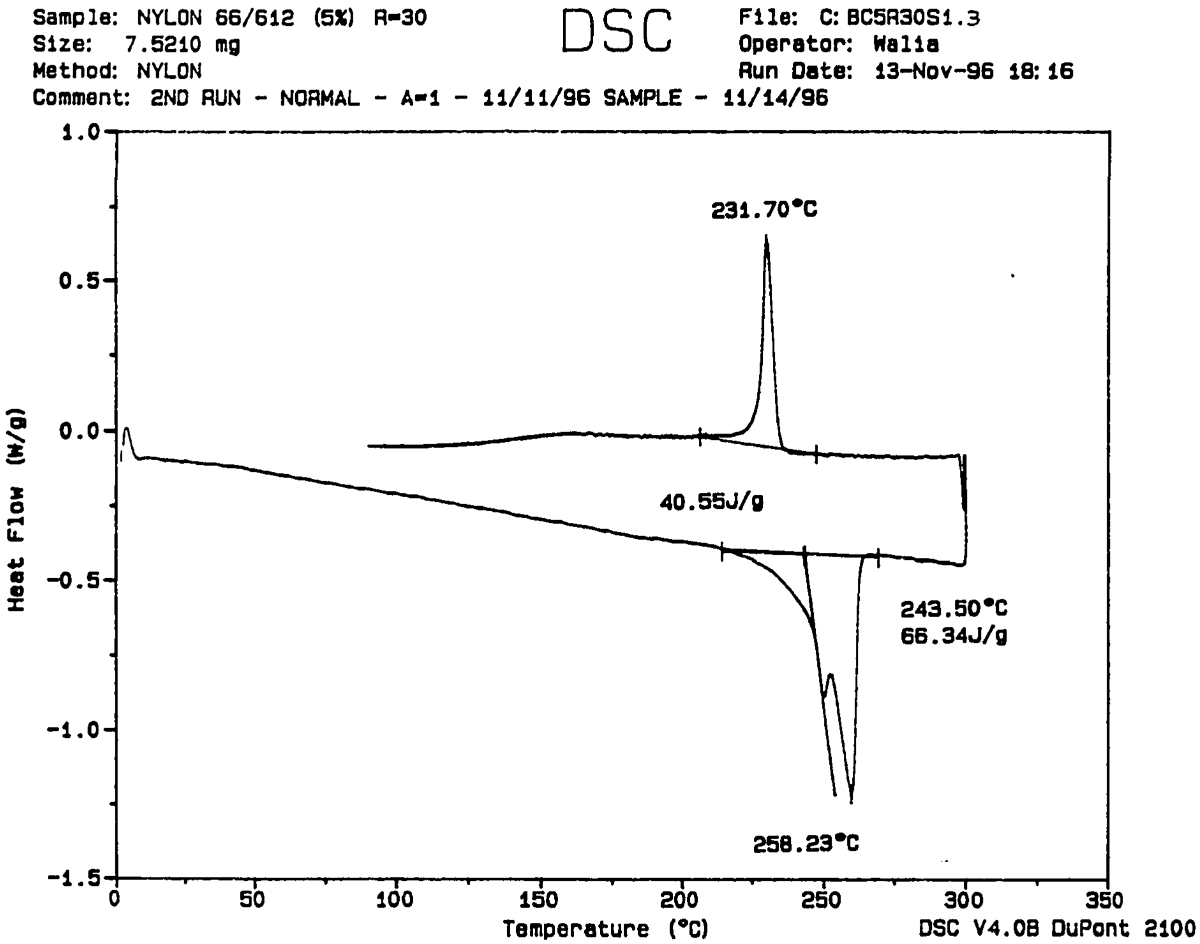


FIGURE B.53: DSC Run for 5% Nylon 6,6/Nylon 6,12, RT=5 min Blend, Annealed for 2 hr (A=2)

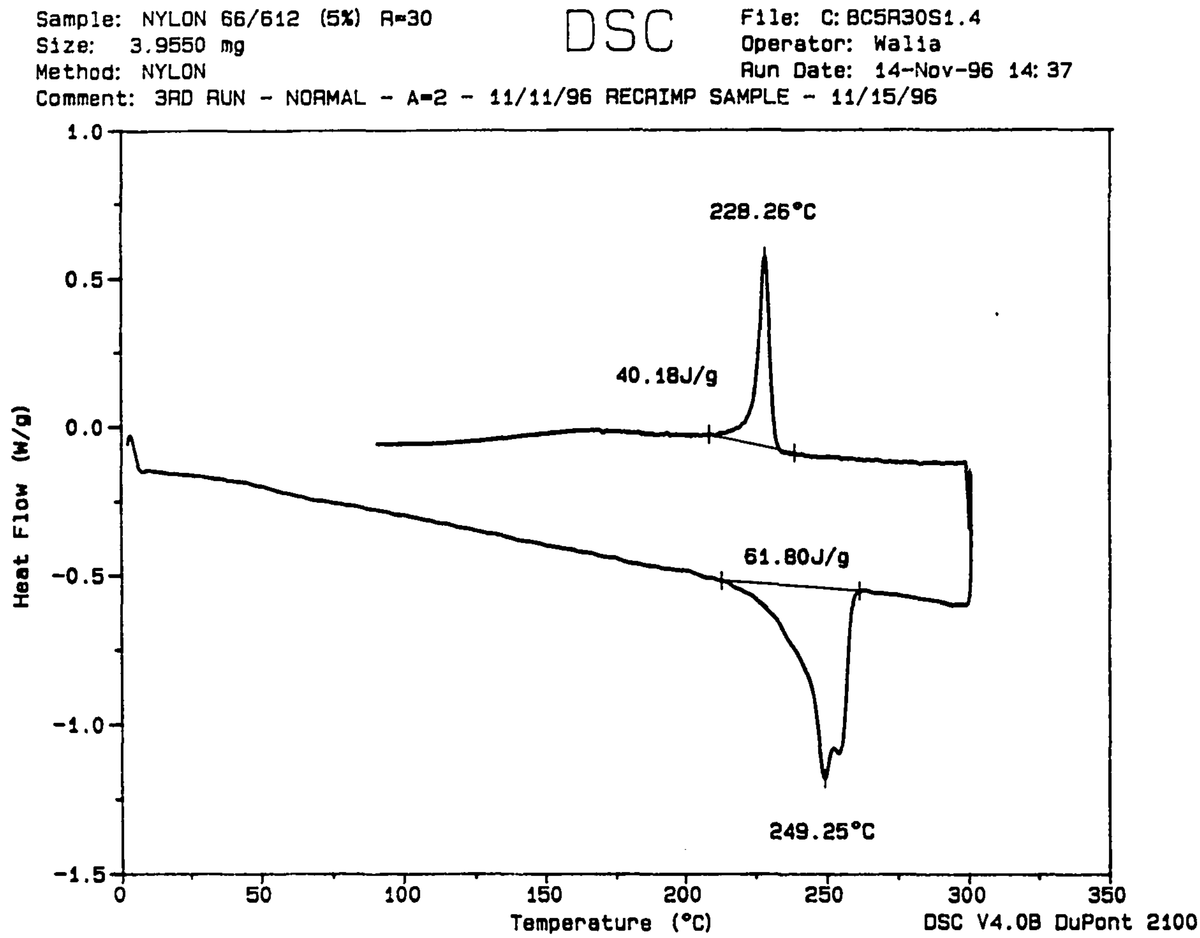


FIGURE B.54: DSC Run for 5% Nylon 6,6/Nylon 6,12, RT=5 min Blend, Annealed for 3 hr (A=3)

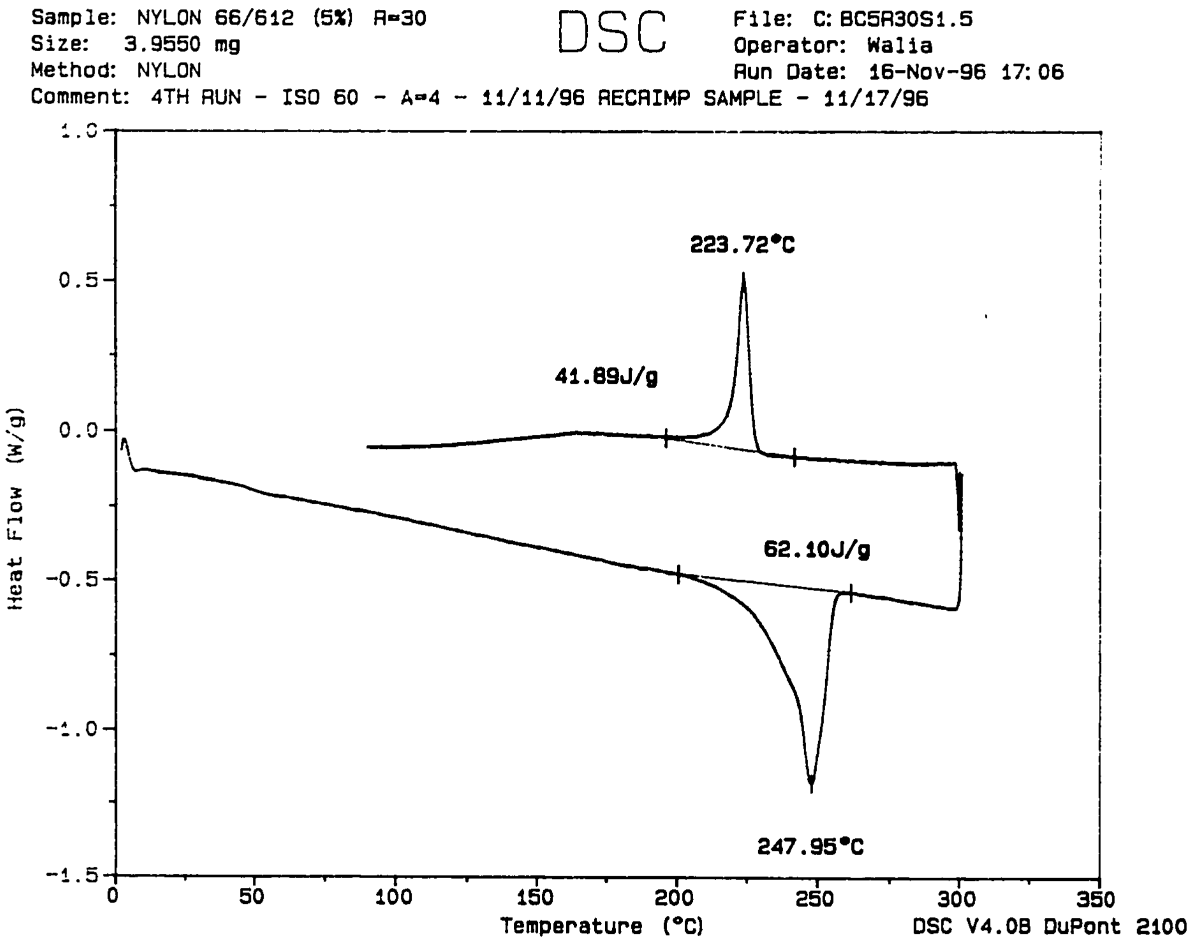


FIGURE B.55: DSC Run for 5% Nylon 6,6/Nylon 6,12, RT=5 min Blend, Annealed for 4 hr (A=4)

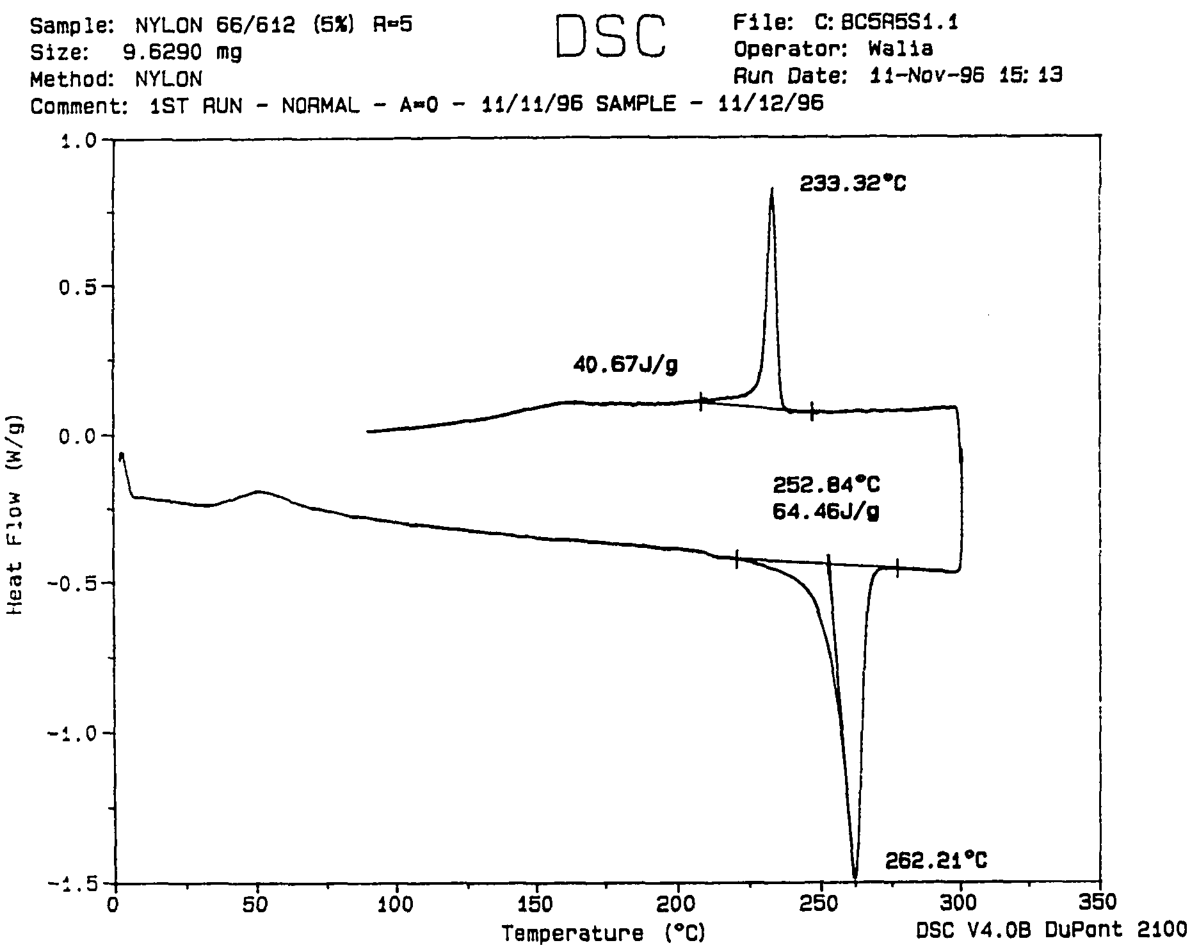


FIGURE B.56: DSC Run for 5% Nylon 6,6/Nylon 6,12, RT=30 min Blend, Unannealed (A=0)

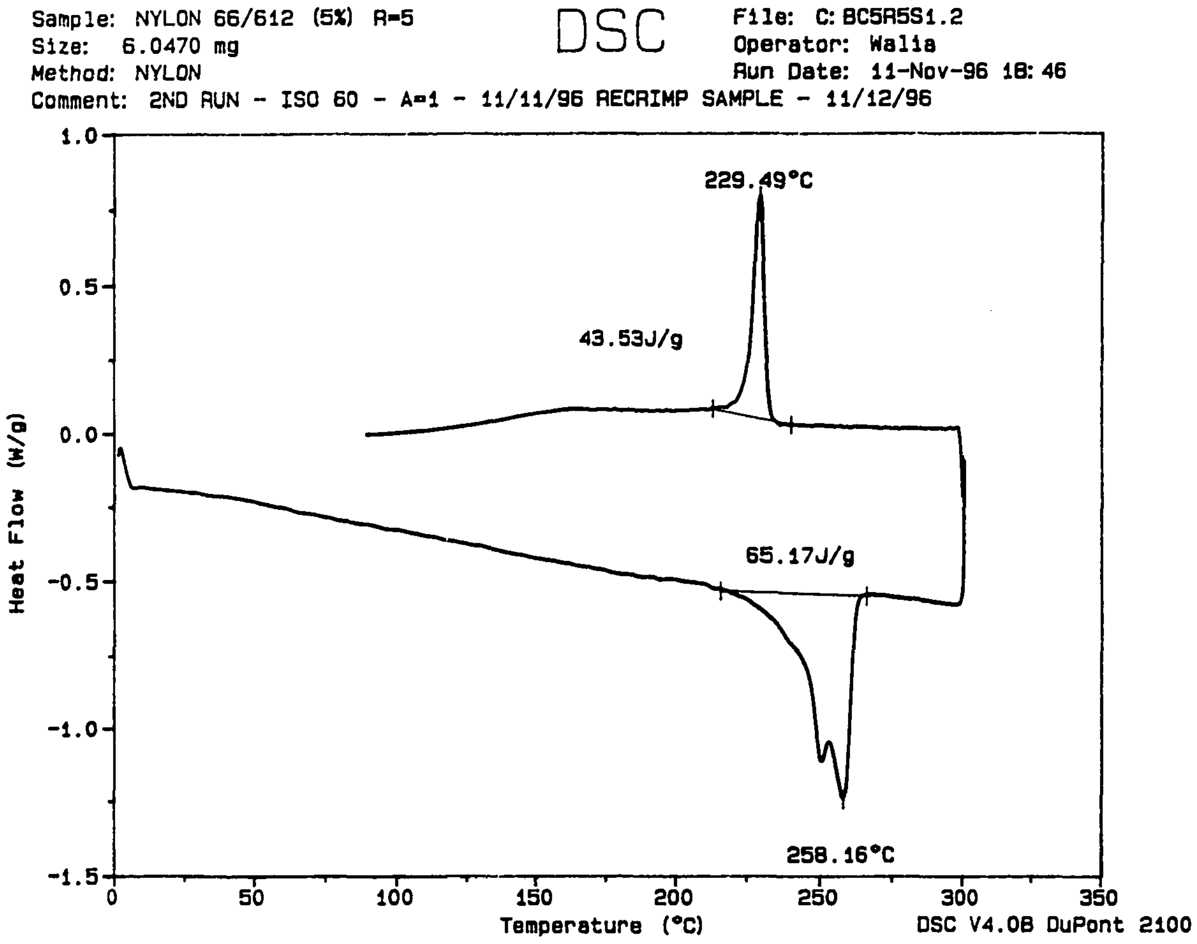


FIGURE B.57: DSC Run for 5% Nylon 6,6/Nylon 6,12, RT=30 min Blend, Annealed for 1 hr (A=1)

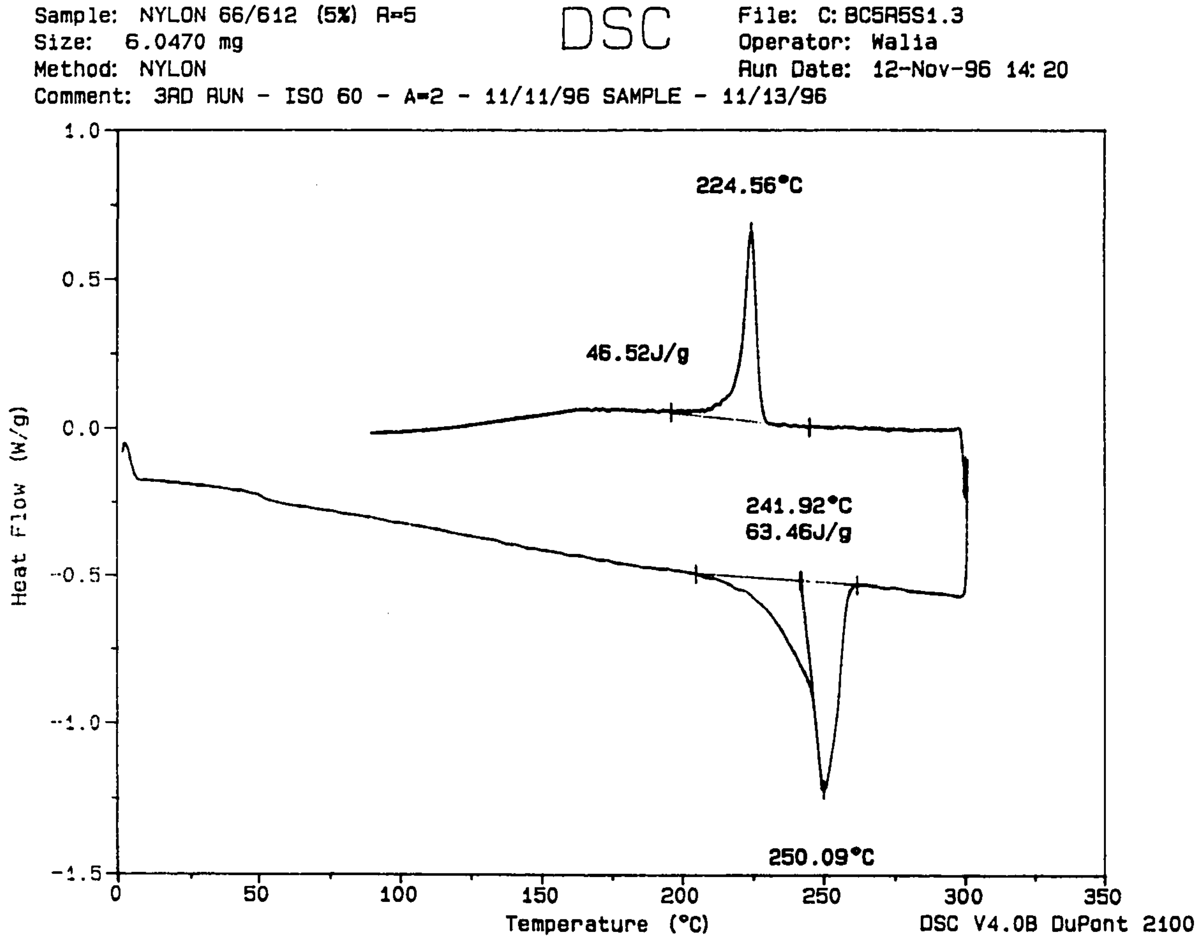


FIGURE B.58: DSC Run for 5% Nylon 6,6/Nylon 6,12, RT=30 min Blend, Annealed for 2 hr (A=2)

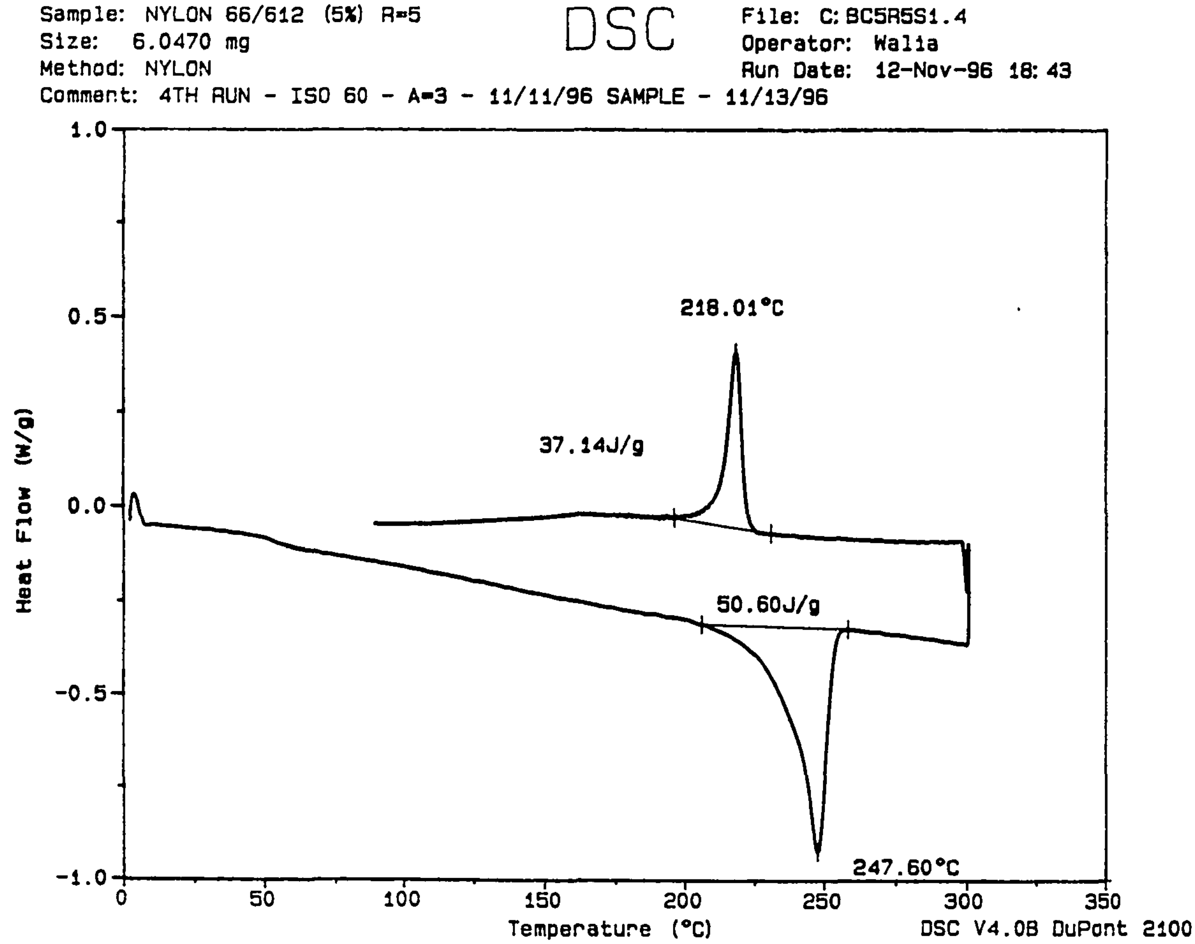


FIGURE B.59: DSC Run for 5% Nylon 6,6/Nylon 6,12, RT=30 min Blend, Annealed for 3 hr (A=3)

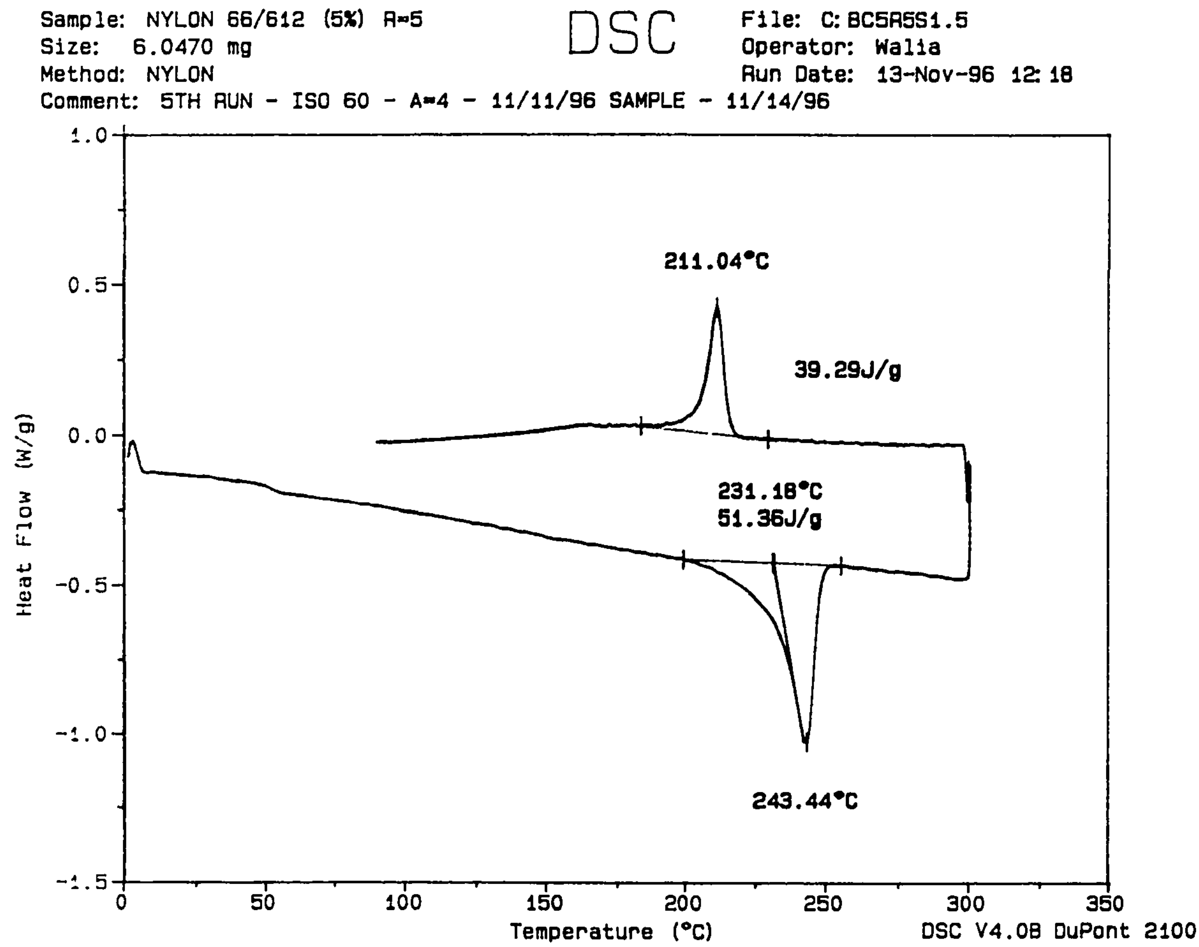


FIGURE B.60: DSC Run for 5% Nylon 6,6/Nylon 6,12, RT=30 min Blend, Annealed for 4 hr (A=4)

APPENDIX C

DSC ISOTHERMAL RUNS OF THE DETAILED EXPERIMENTATION STAGE

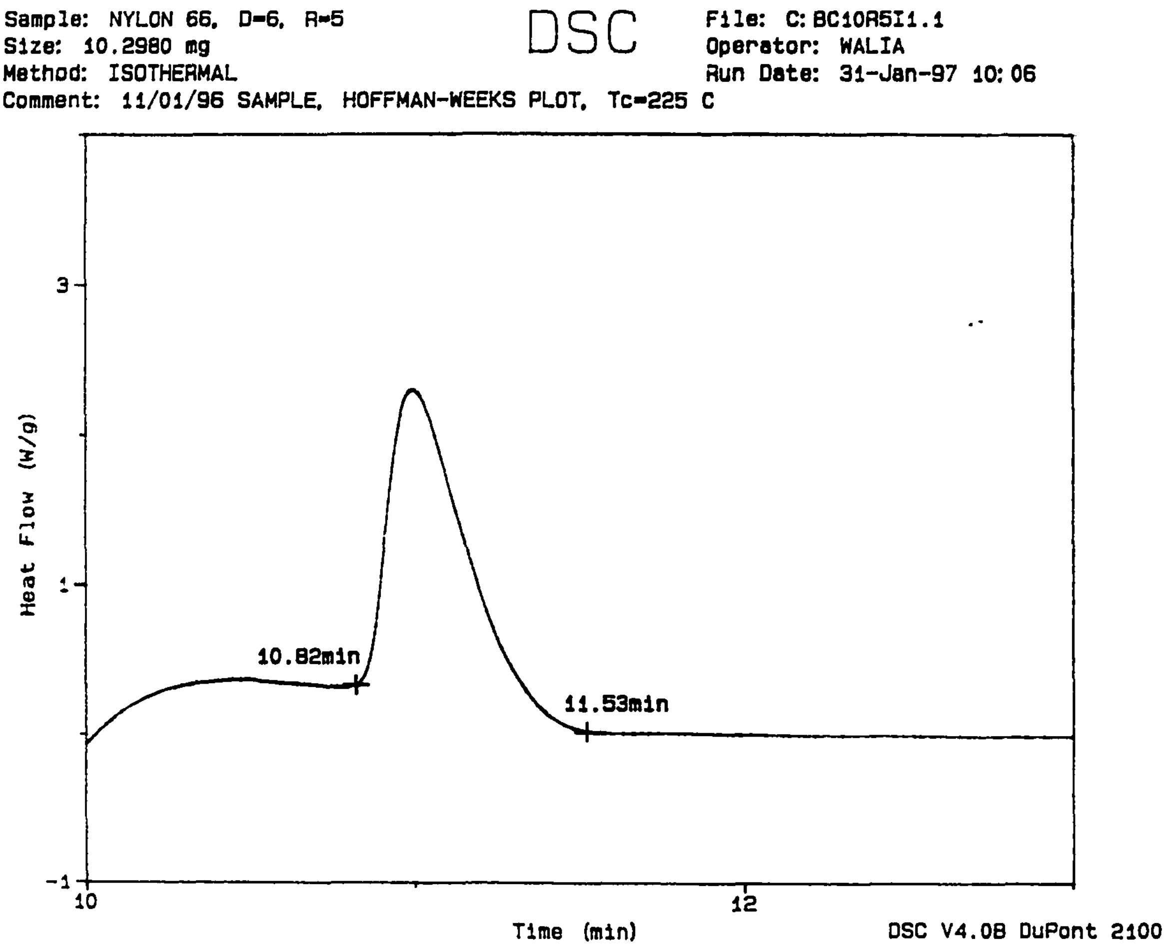
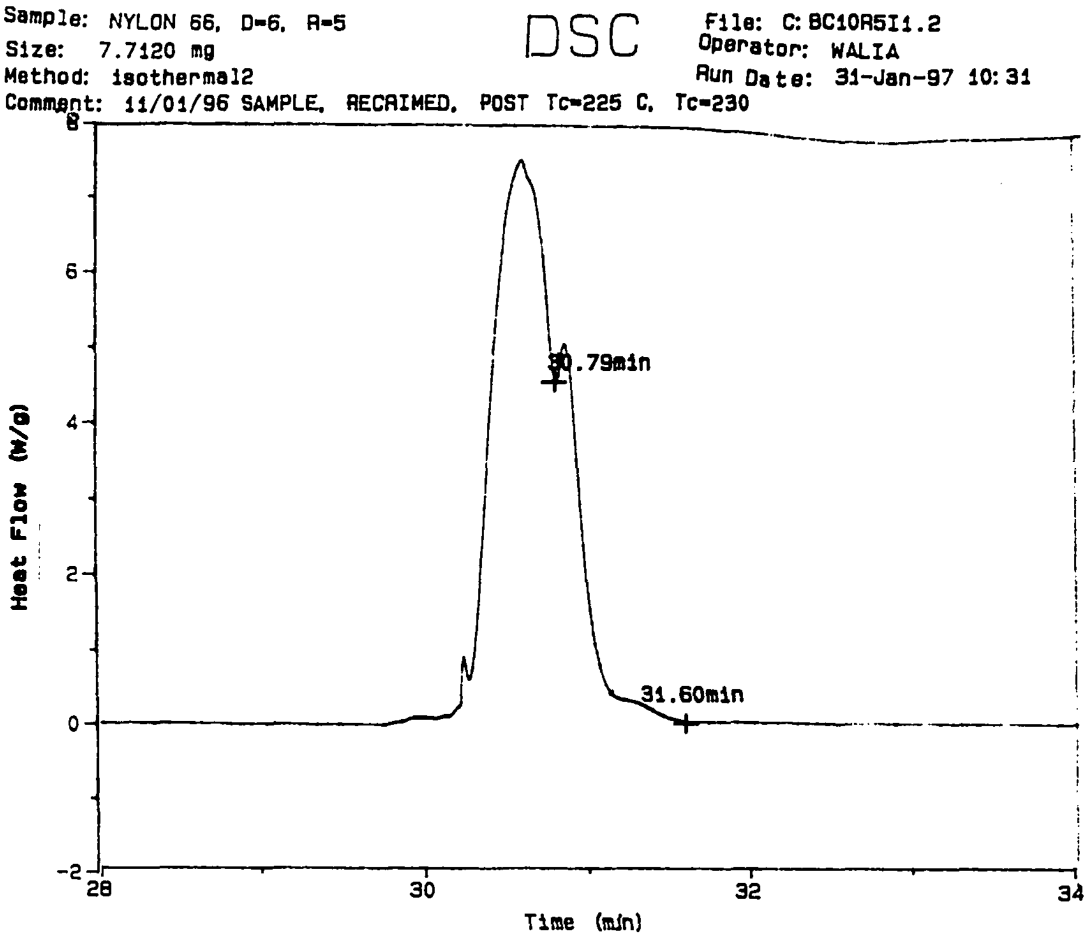


FIGURE C.1: Isothermal Run for Pure Nylon 6,6 at 225°C



Sample: NYLON 66, D=6, R=5
Size: 7.7120 mg
Method: isothermal2
Comment: 11/01/96 SAMPLE, RECRIMED, POST Tc=225 C, Tc=230

DSC

File: C:BC10R5I1.2
Operator: WALIA
Run Date: 31-Jan-97 10:31

FIGURE C.2: Isothermal Run for Pure Nylon 6,6 at 230°C

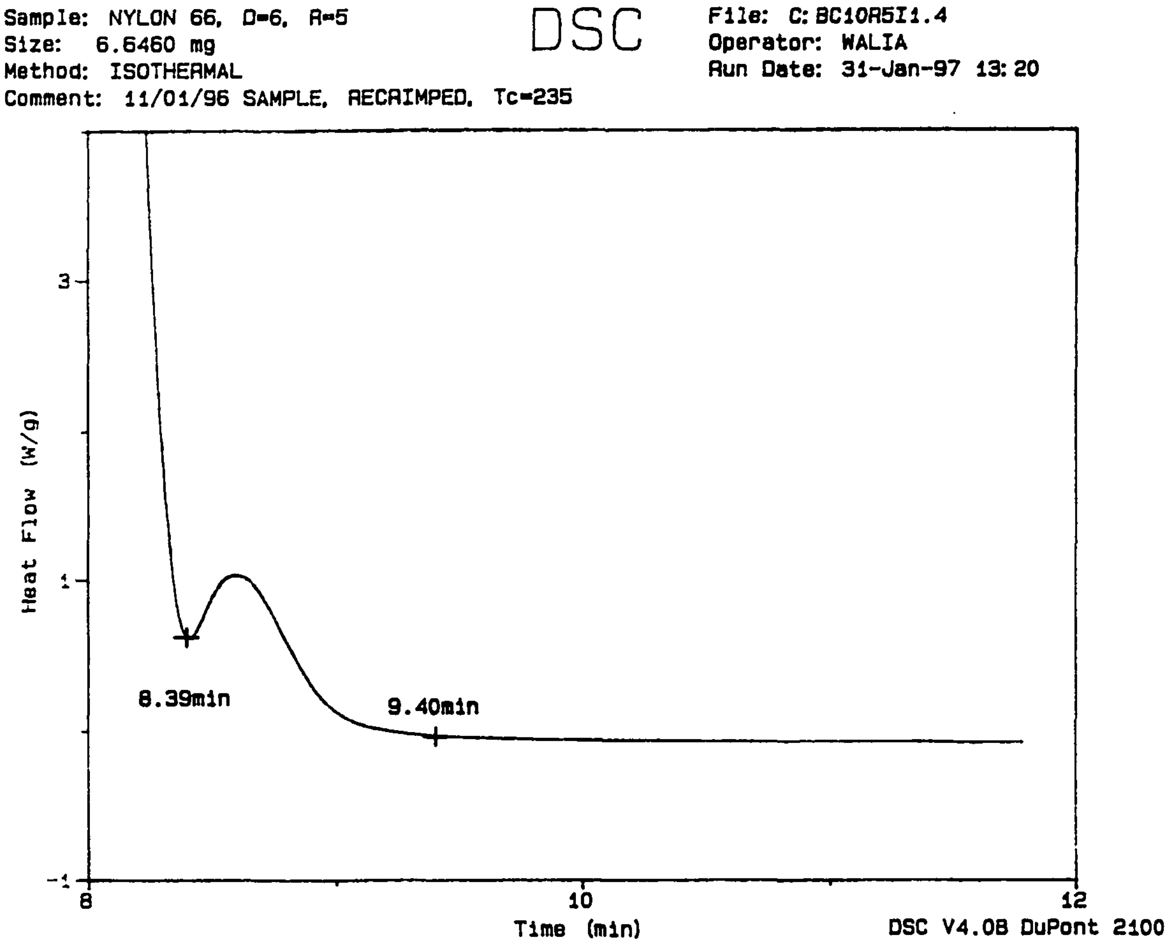


FIGURE C.3: Isothermal Run for Pure Nylon 6,6 at 235°C

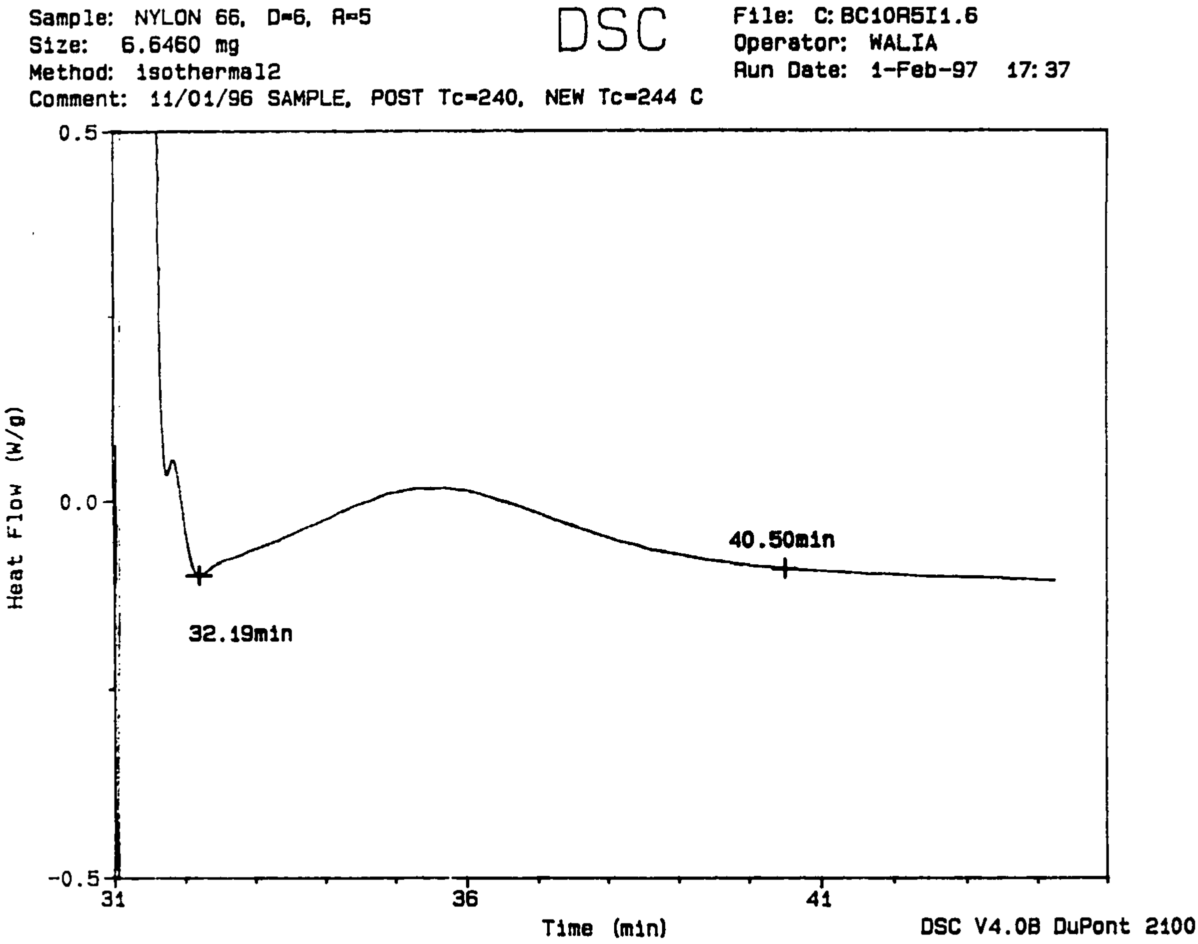


FIGURE C.4: Isothermal Run for Pure Nylon 6,6 at 244°C

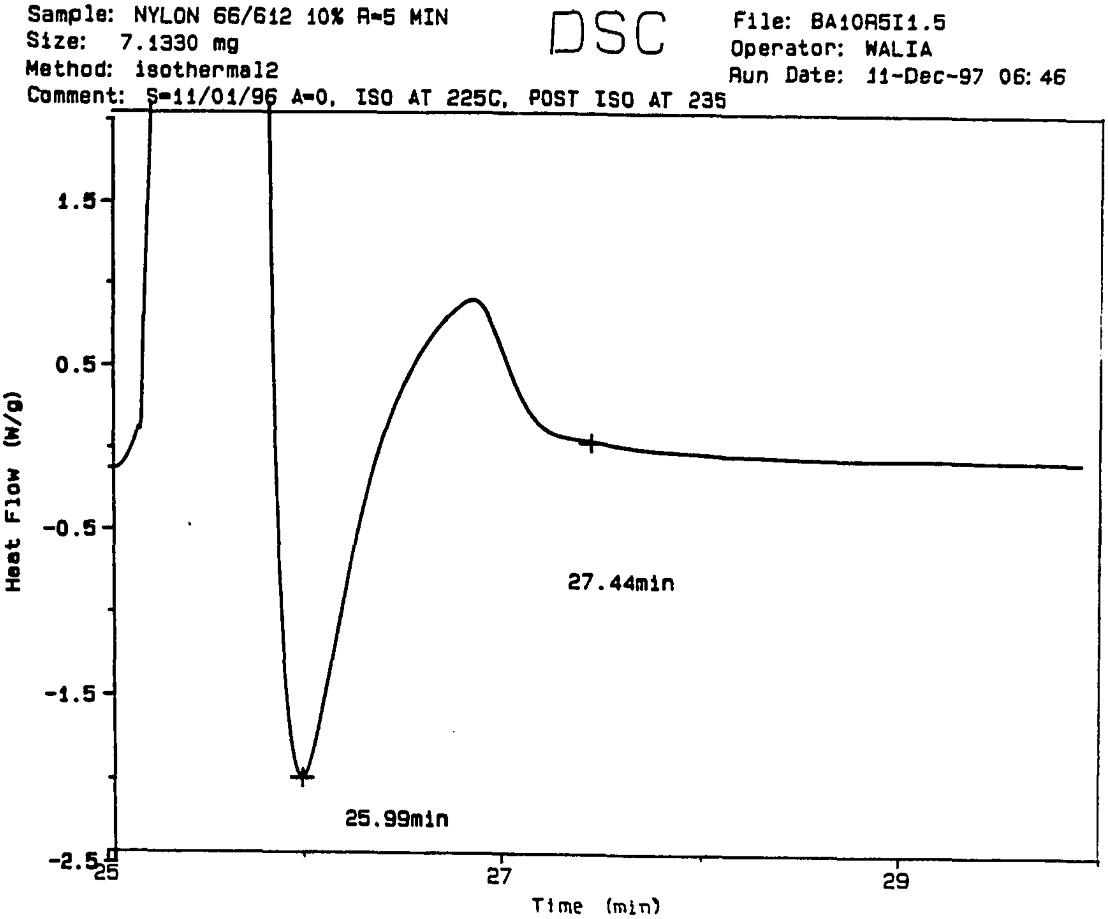


FIGURE C.5: Isothermal Run for 10% Nylon 6,6/Trogamid-T, RT=5 min Blend, Unannealed (A=0) at 225°C

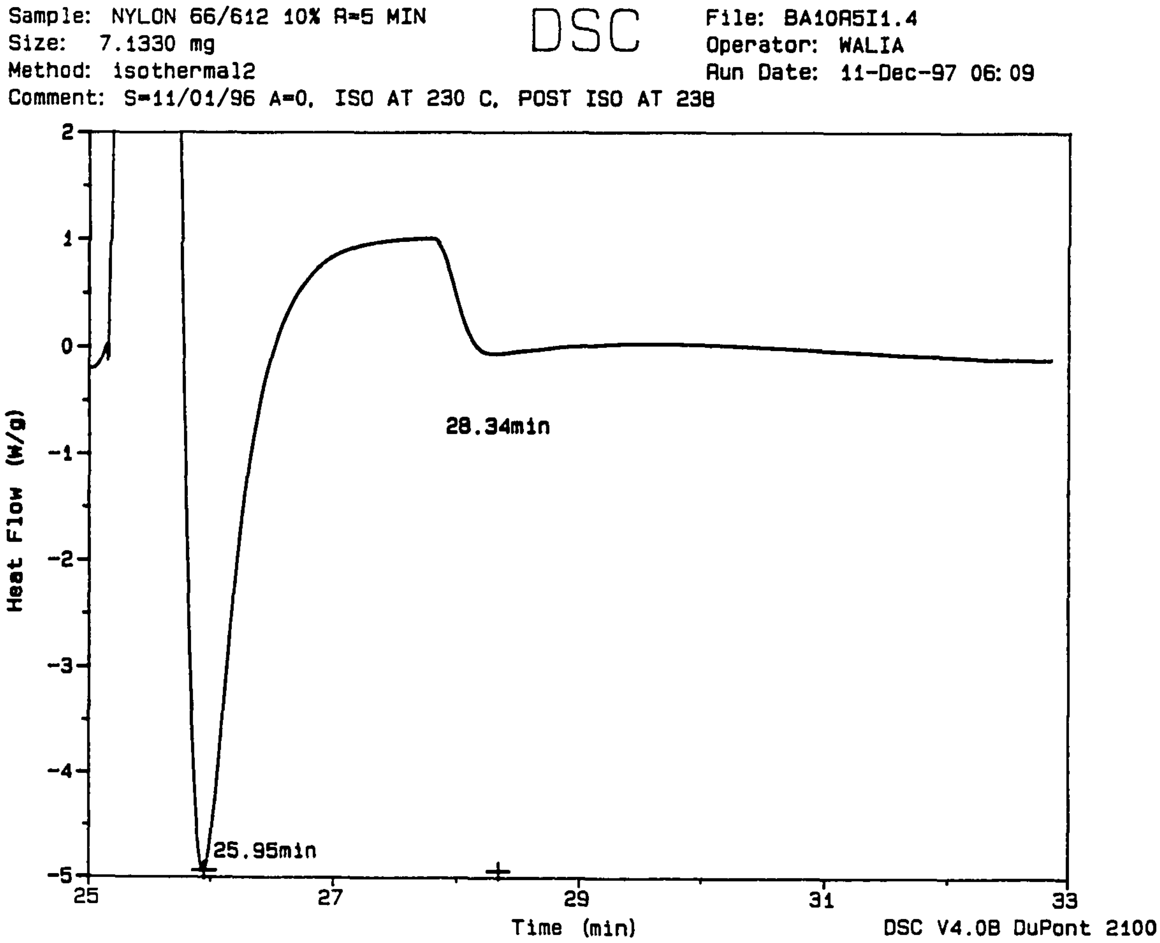


FIGURE C.6: Isothermal Run for 10% Nylon 6,6/Trogamid-T, RT=5 min Blend, Unannealed (A=0) at 230°C

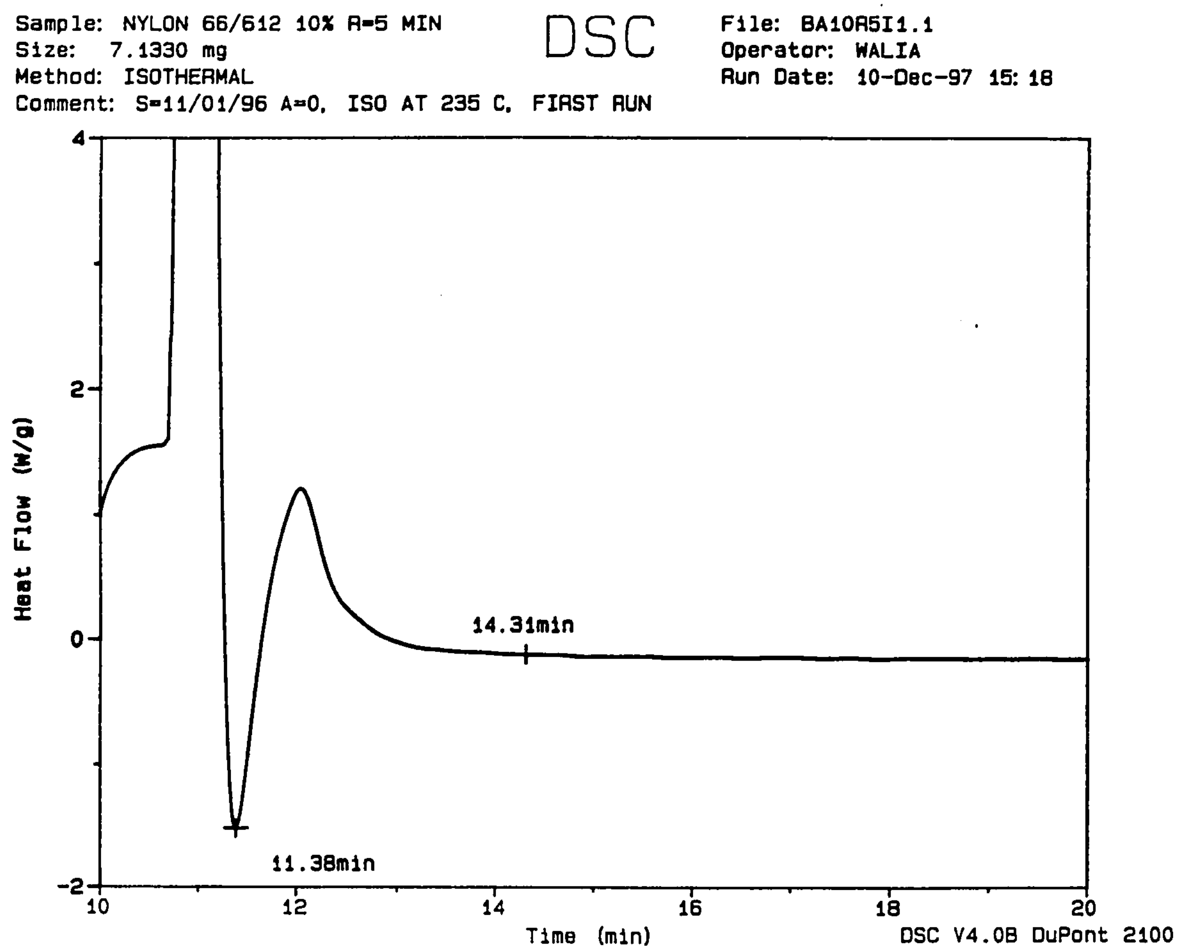


FIGURE C.7: Isothermal Run for 10% Nylon 6,6/Trogamid-T, RT=5 min Blend, Unannealed (A=0) at 235°C

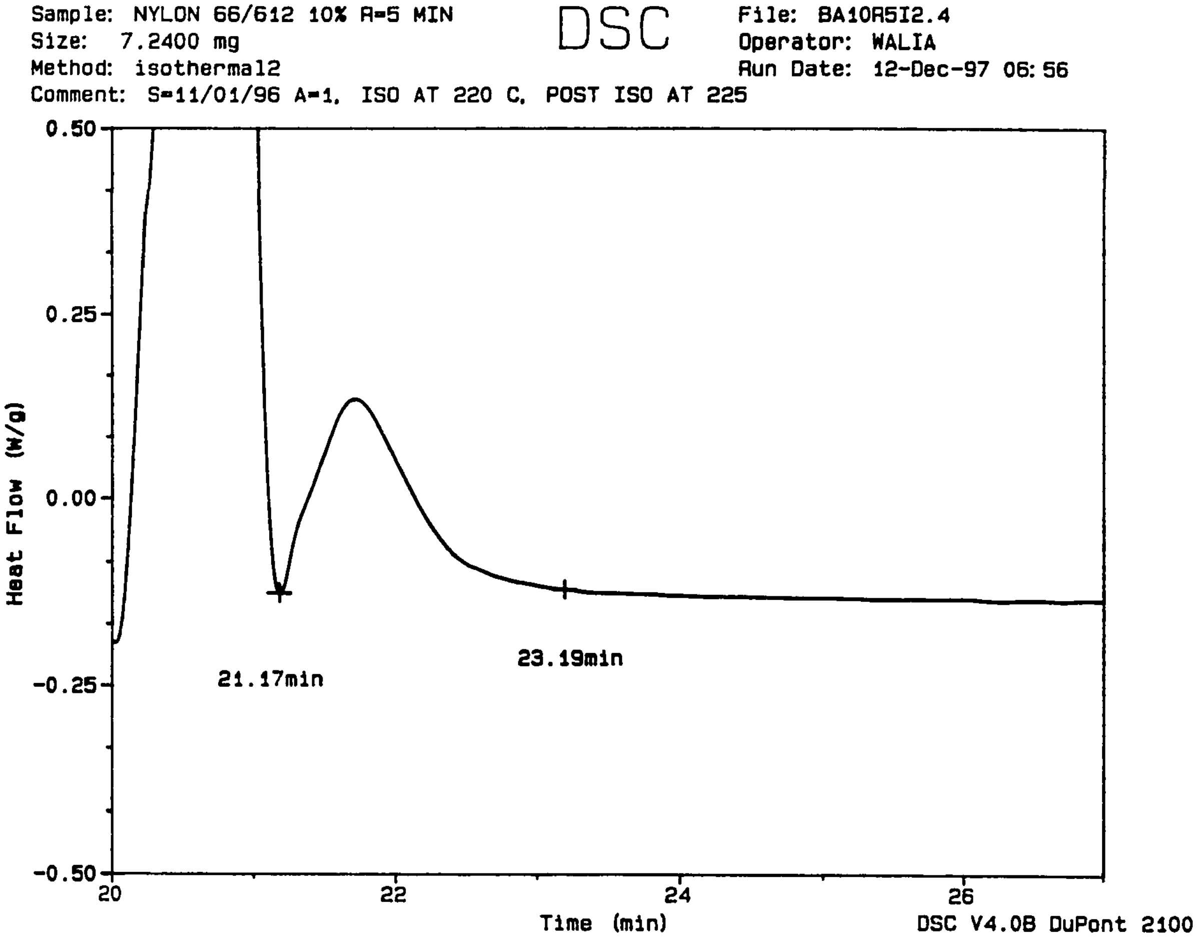


FIGURE C.8: Isothermal Run for 10% Nylon 6,6/Trogamid-T, RT=5 min Blend, Annealed for 1 hr (A=1) at 220°C

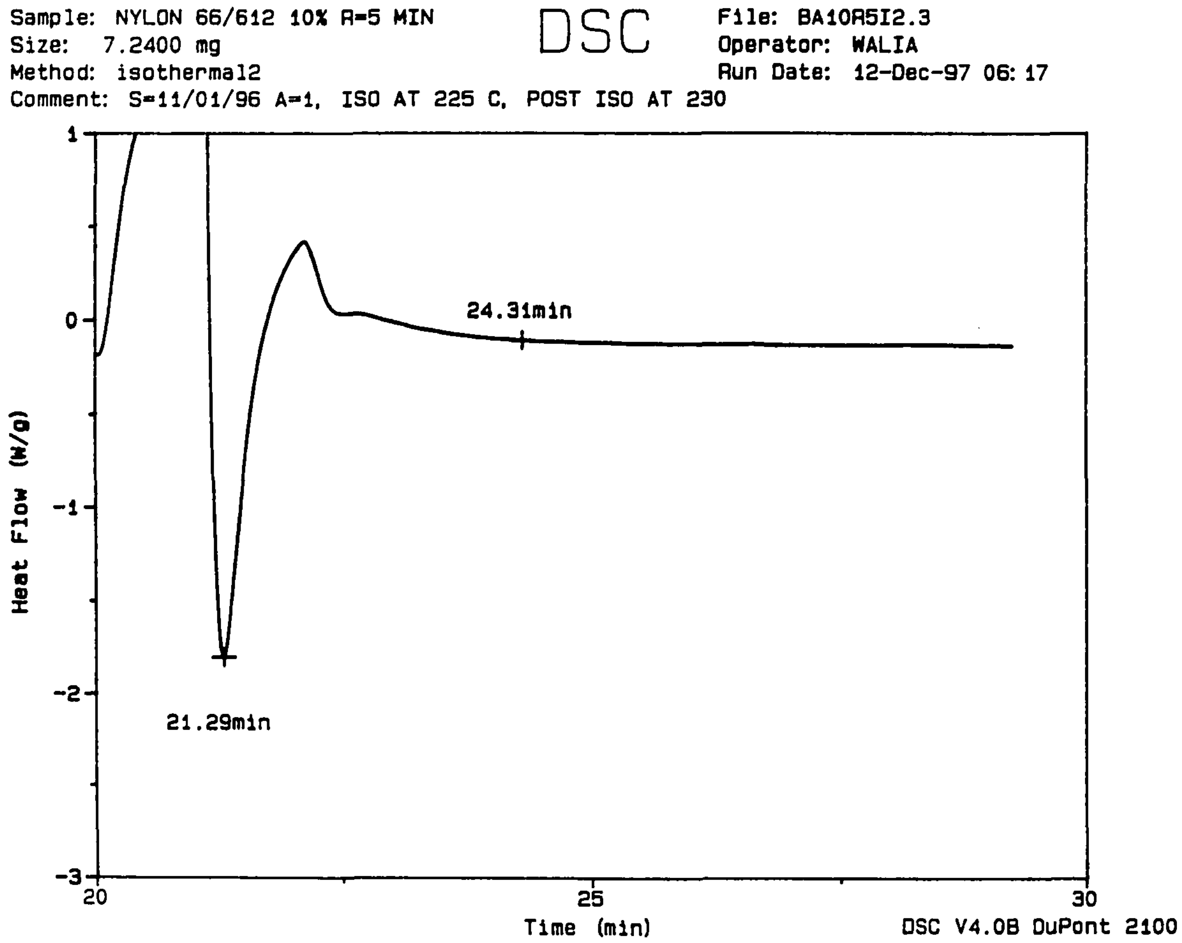


FIGURE C.9: Isothermal Run for 10% Nylon 6,6/Trogamid-T, RT=5 min Blend, Annealed for 1 hr (A=1) at 225°C

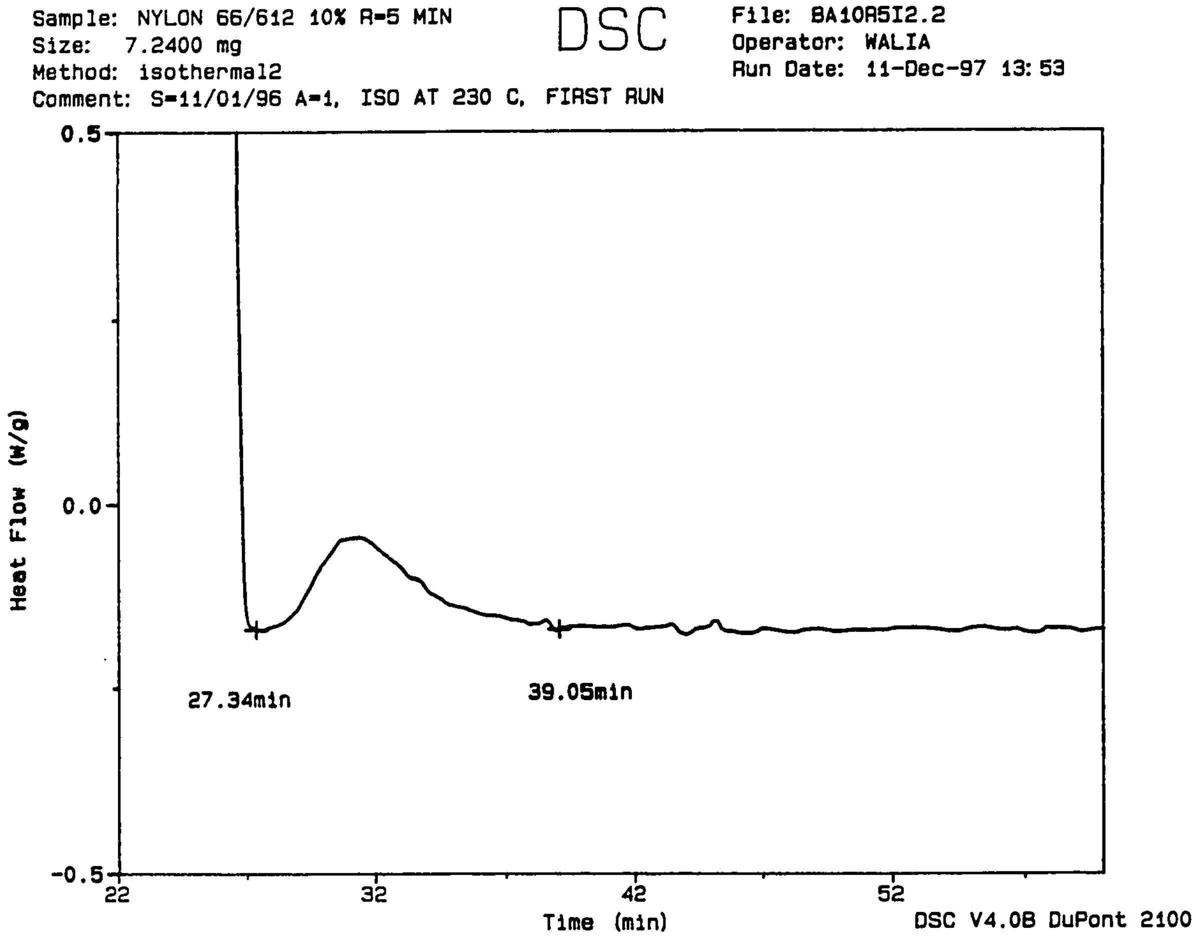


FIGURE C.10: Isothermal Run for 10% Nylon 6,6/Trogamid-T, RT=5 min Blend, Annealed for 1 hr (A=1) at 230°C

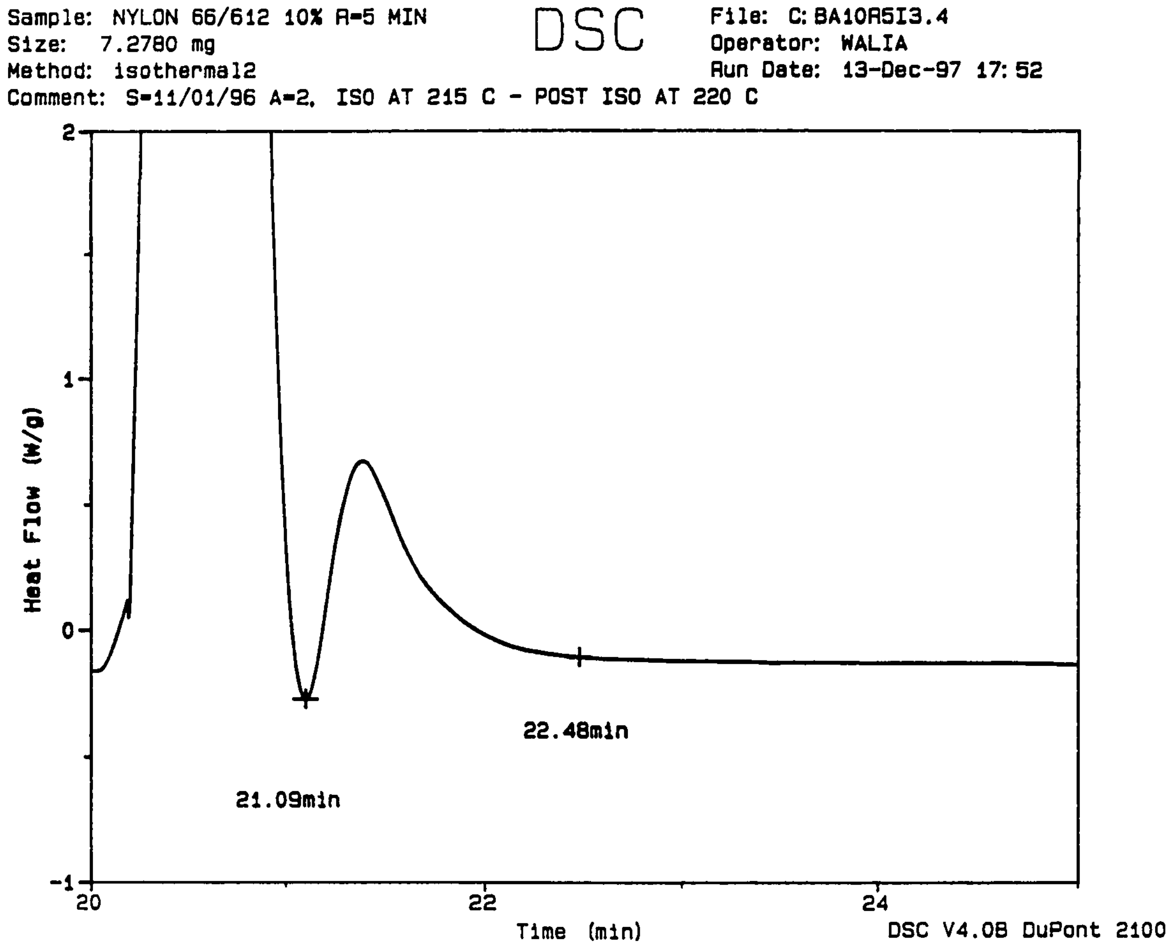


FIGURE C.11: Isothermal Run for 10% Nylon 6,6/Trogamid-T, RT=5 min Blend, Annealed for 2 hrs (A=2) at 215°C

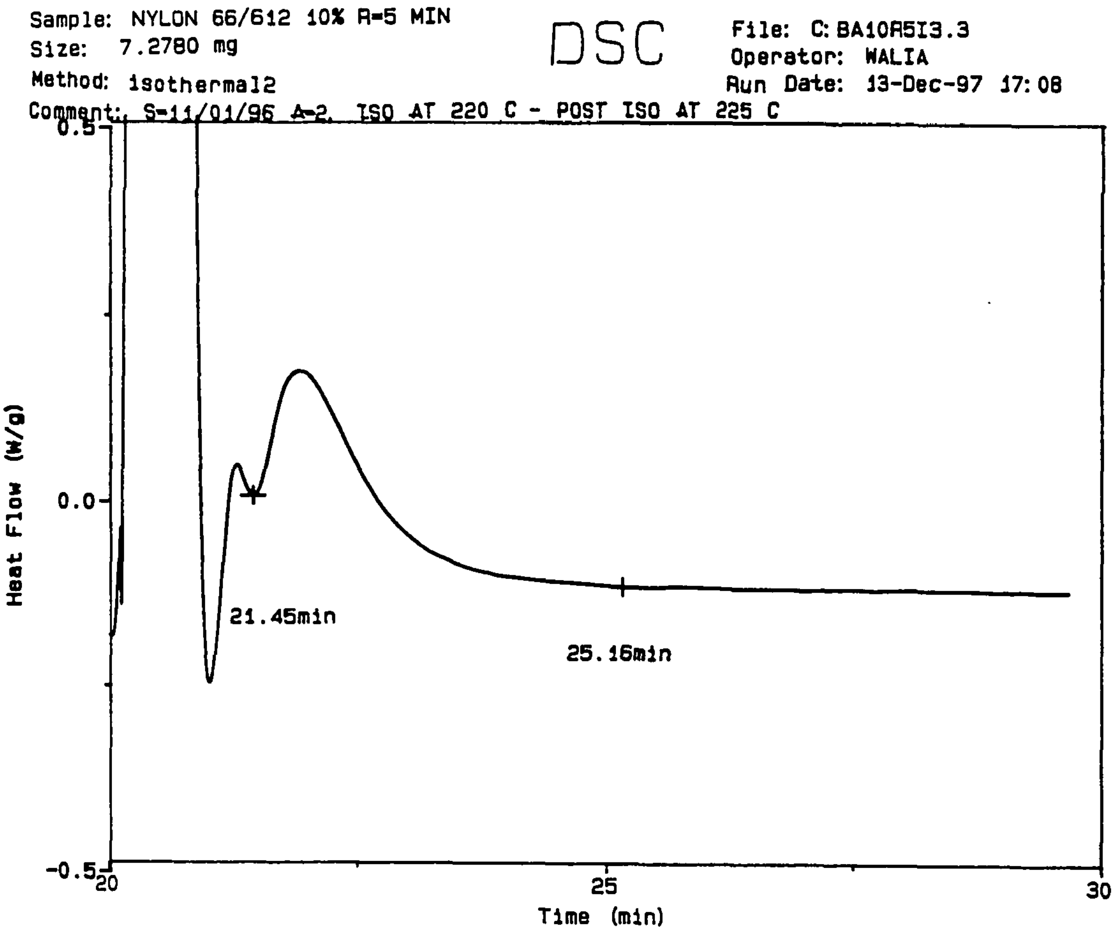


FIGURE C.12: Isothermal Run for 10% Nylon 6,6/Trogamid-T, RT=5 min, Annealed for 2 hrs (A=2) at 220°C

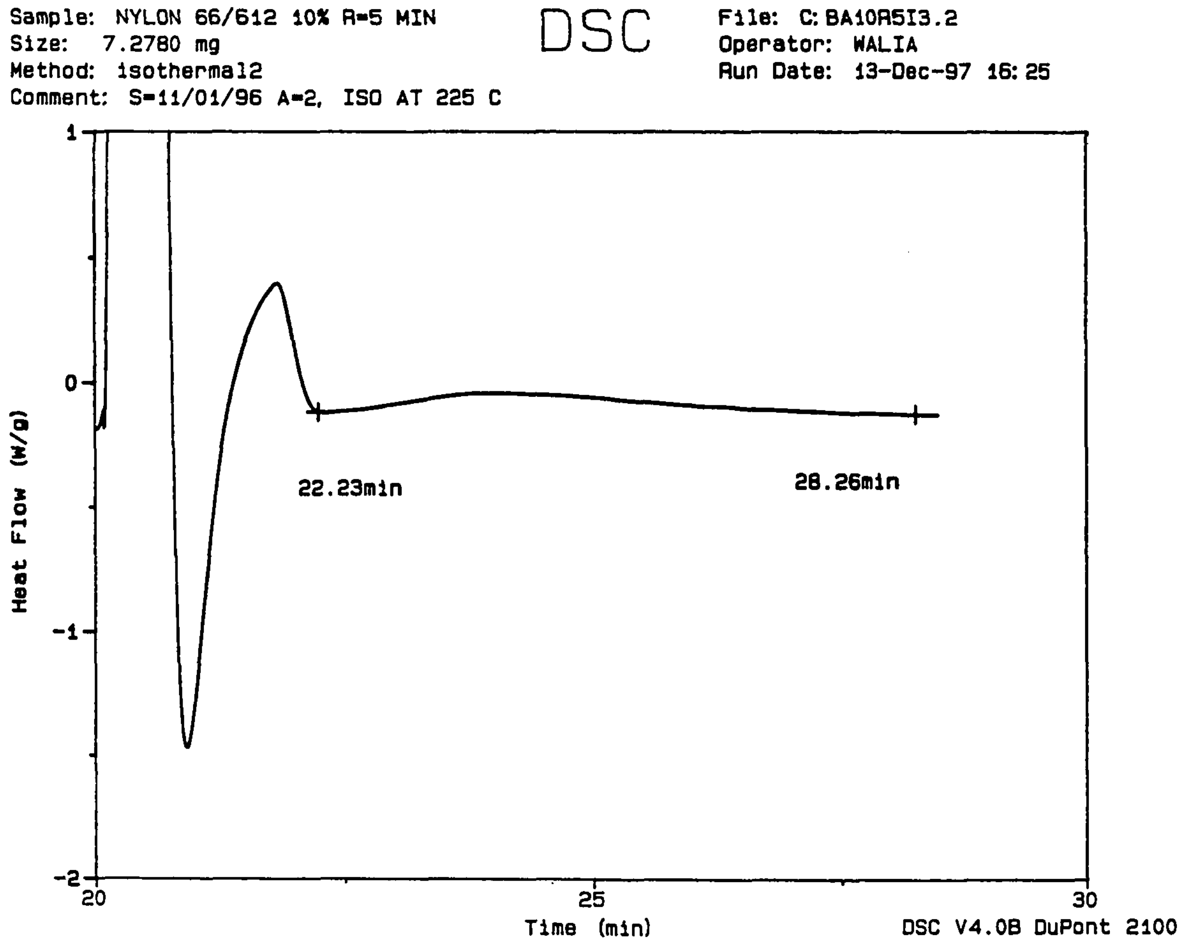


FIGURE C.13: Isothermal Run for 10% Nylon 6,6/Trogamid-T, RT=5 min Blend, Annealed for 2 hrs (A=2) at 225°C

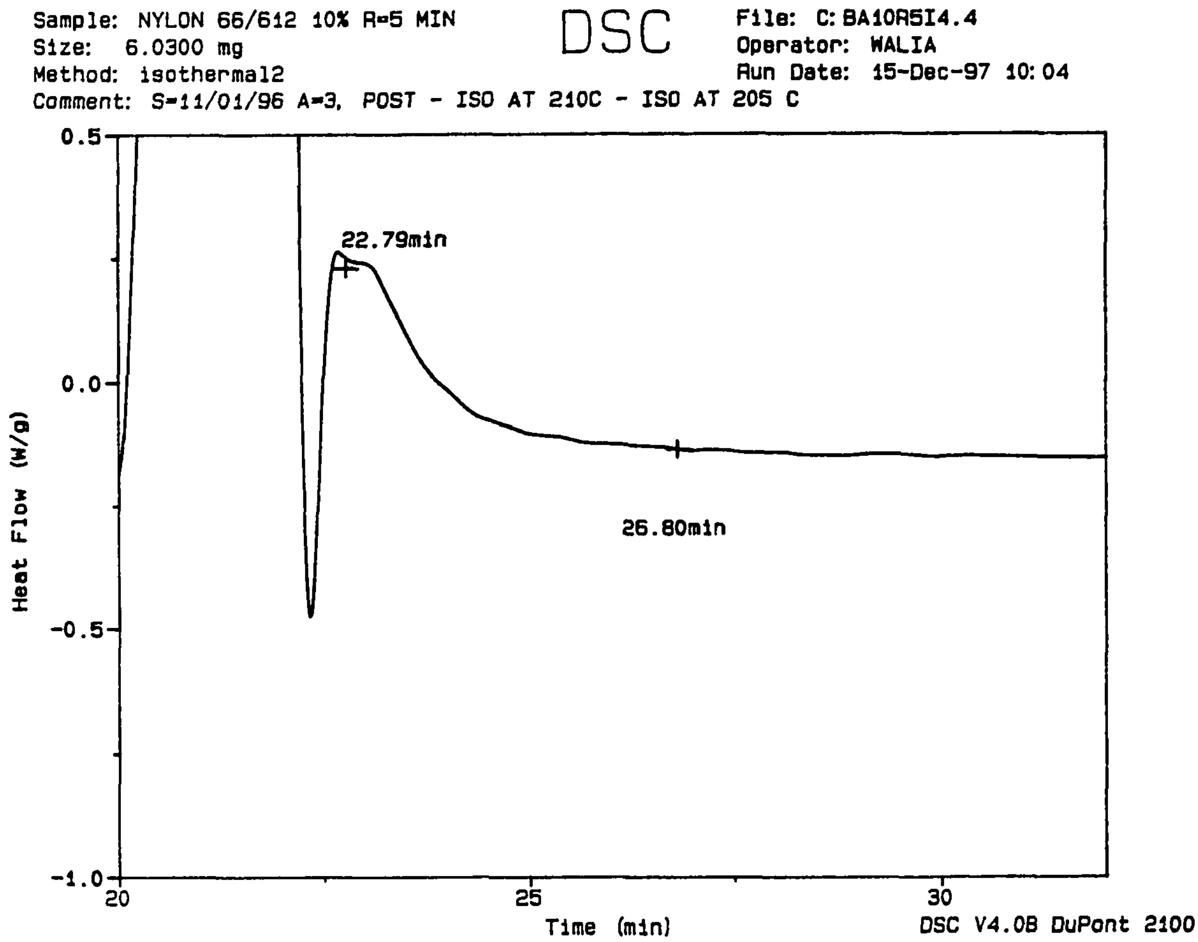


FIGURE C.14: Isothermal Run for 10% Nylon 6,6/Trogamid-T, RT=5 min Blend, Annealed for 3 hrs (A=3) at 205°C

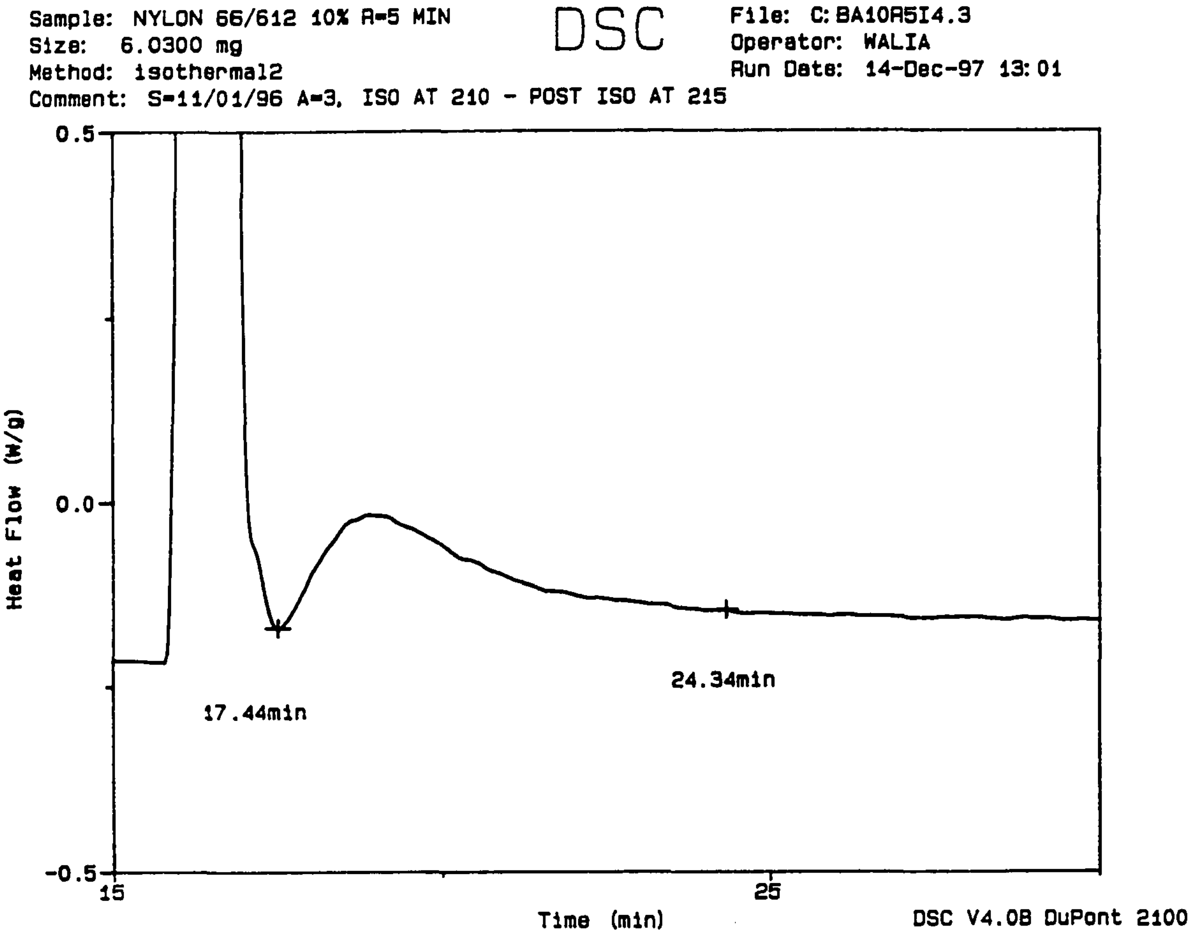


FIGURE C.15: Isothermal Run for 10% Nylon 6,6/Trogamid-T, RT=5 min Blend, Annealed for 3 hrs (A=3) at 210°C

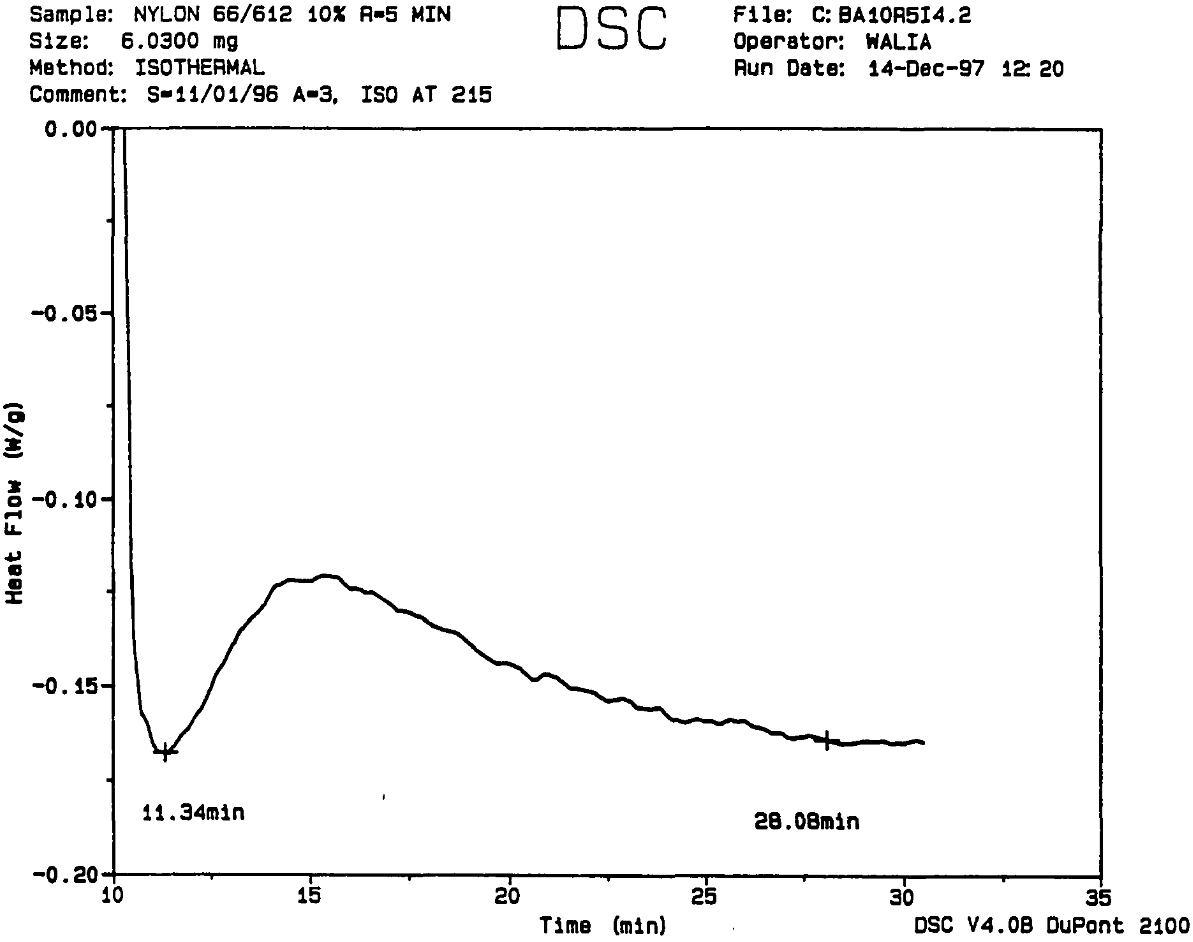


FIGURE C.16: Isothermal Run for 10% Nylon 6,6/Trogamid-T, RT=5 min Blend, Annealed for 3 hrs (A=3) at 215°C

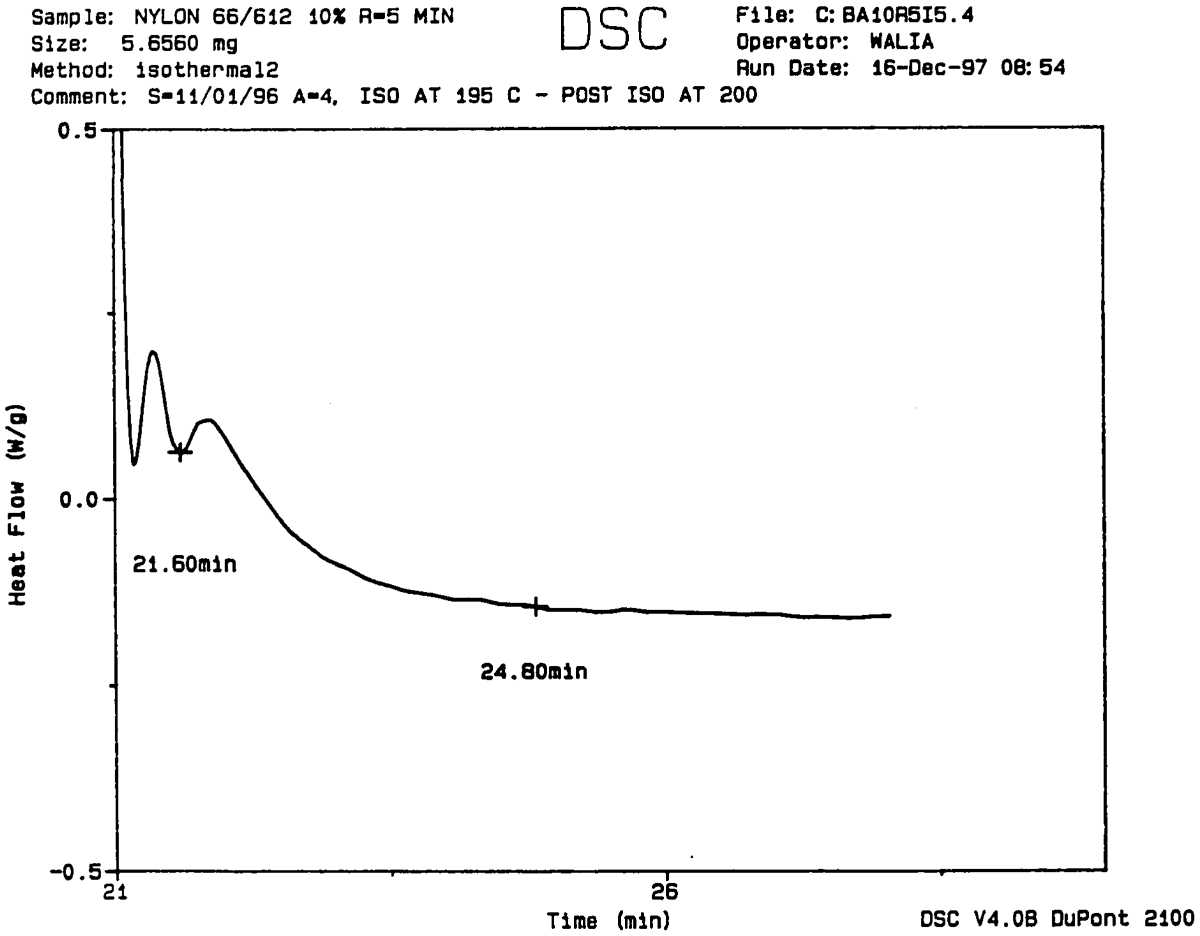


FIGURE C.17: Isothermal Run for 10% Nylon 6,6/Trogamid-T, RT=5 min Blend, Annealed for 4 hrs (A=4) at 195°C

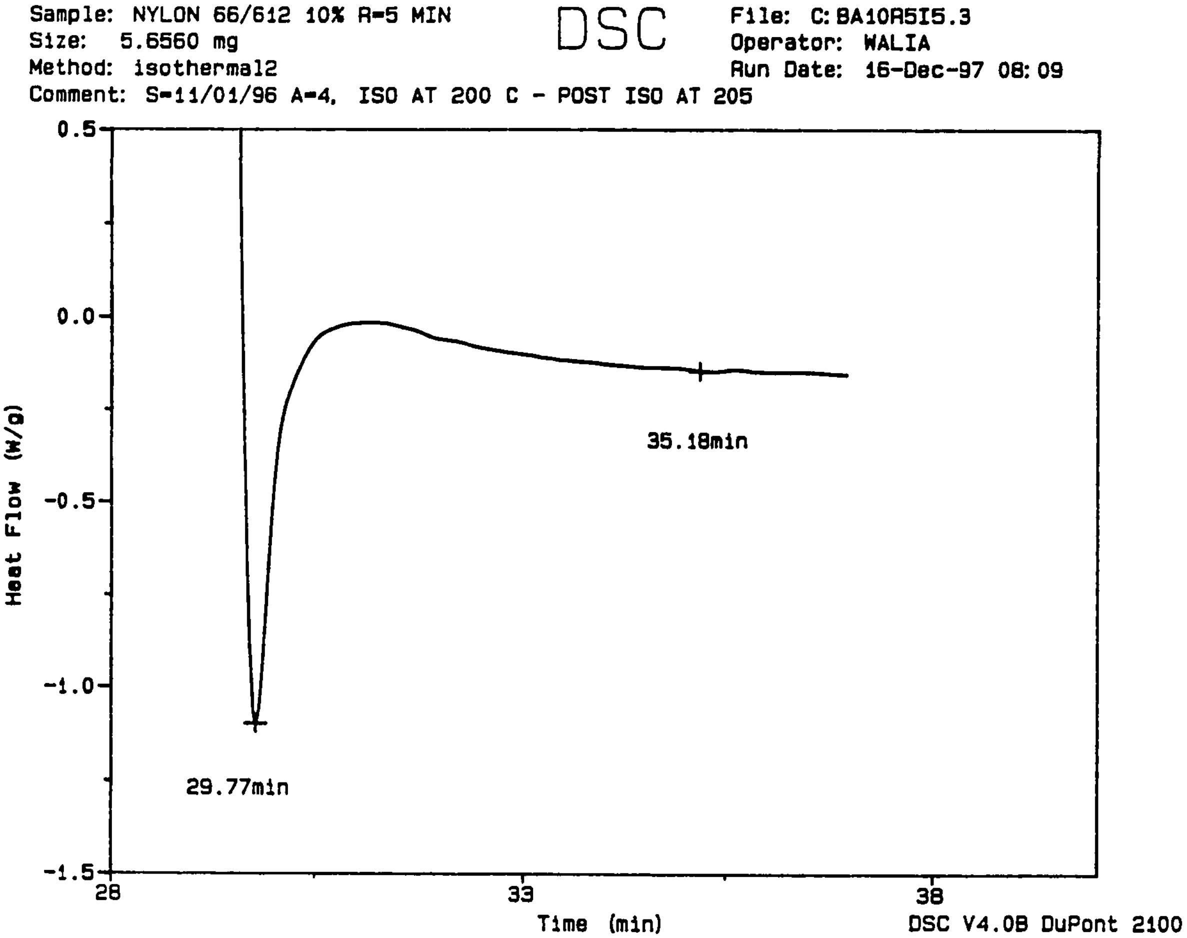


FIGURE C.18: Isothermal Run for 10% Nylon 6,6/Trogamid-T, RT=5 min Blend, Annealed for 4 hrs (A=4) at 200°C

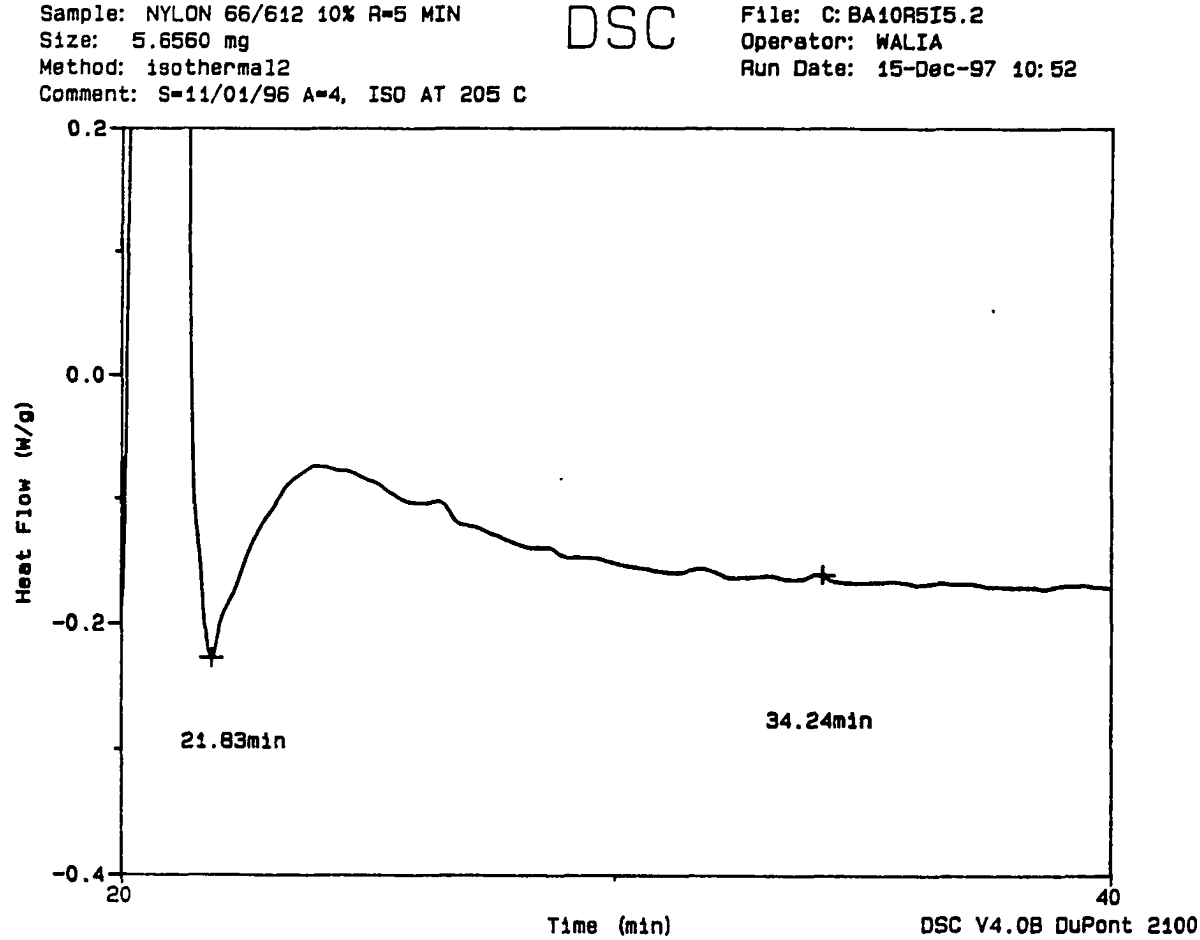


FIGURE C.19: Isothermal Run for 10% Nylon 6,6/Trogamid-T, RT=5 min Blend, Annealed for 4 hrs (A=4) at 205°C

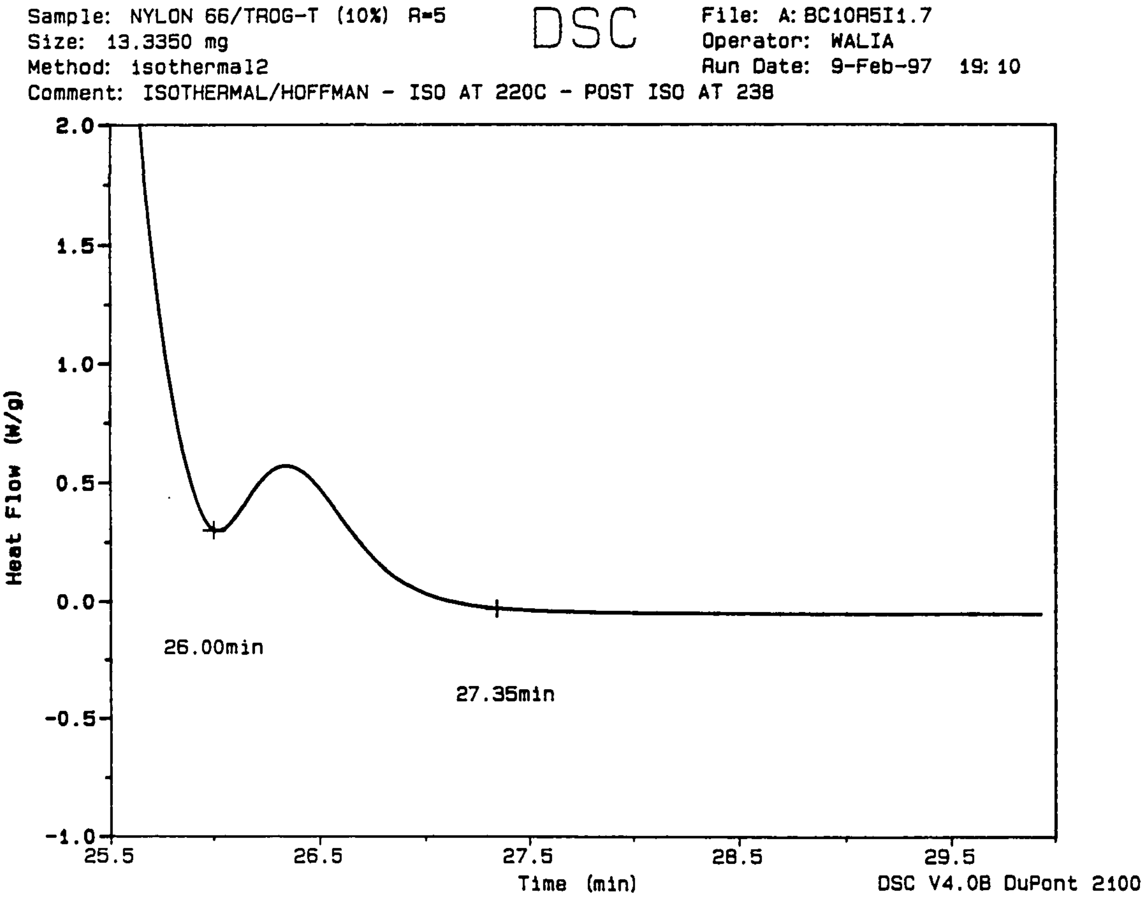
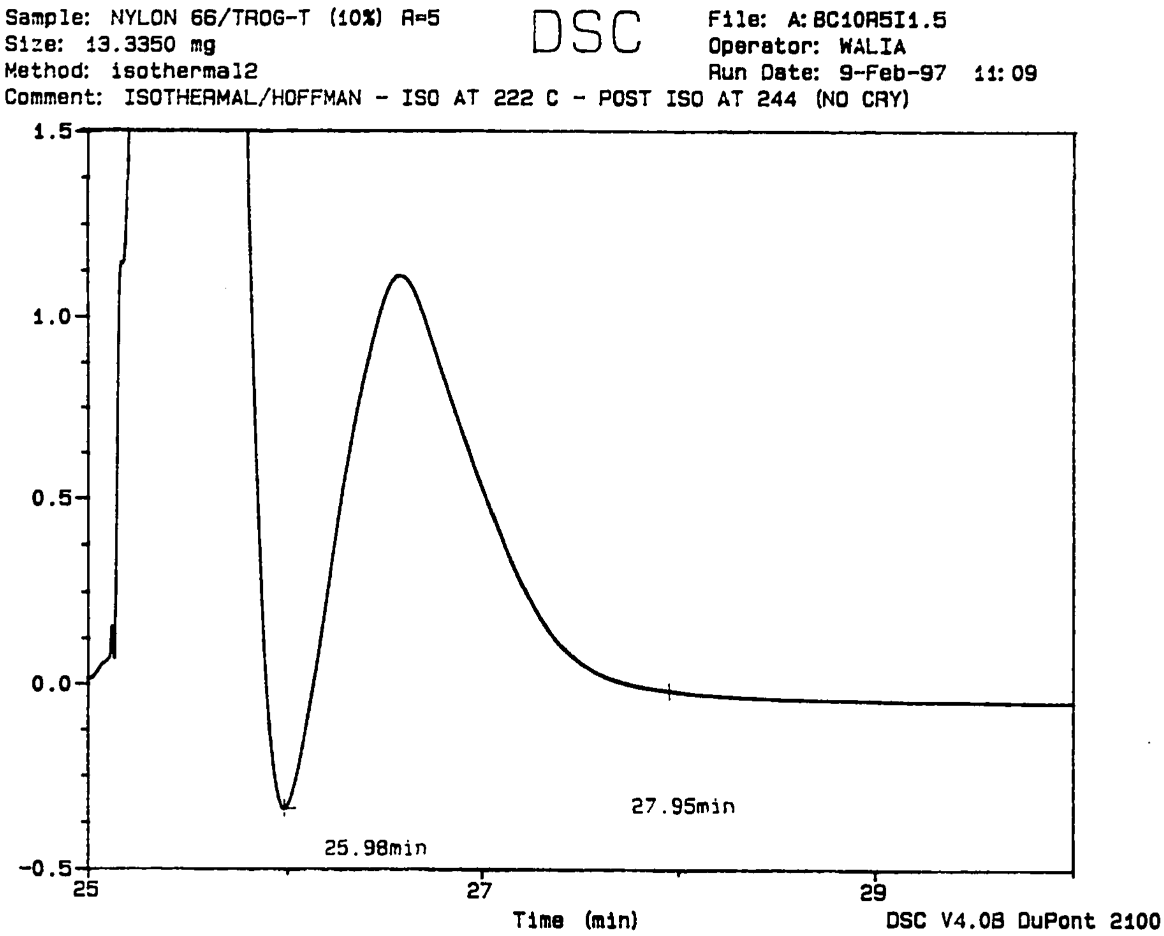


FIGURE C.20: Isothermal Run for 10% Nylon 6,6/Nylon 6,12, RT=5 min Blend, Unannealed (A=0) at 220°C



Sample: NYLON 66/TROG-T (10%) A=5
Size: 13.3350 mg
Method: isothermal2
Comment: ISOTHERMAL/HOFFMAN - ISO AT 222 C - POST ISO AT 244 (NO CRY)

DSC

File: A:8C10A5I1.5
Operator: WALIA
Run Date: 9-Feb-97 11:09

FIGURE C.21: Isothermal Run for 10% Nylon 6,6/Nylon 6,12, RT=5 min Blend, Unannealed (A=0) at 225°C

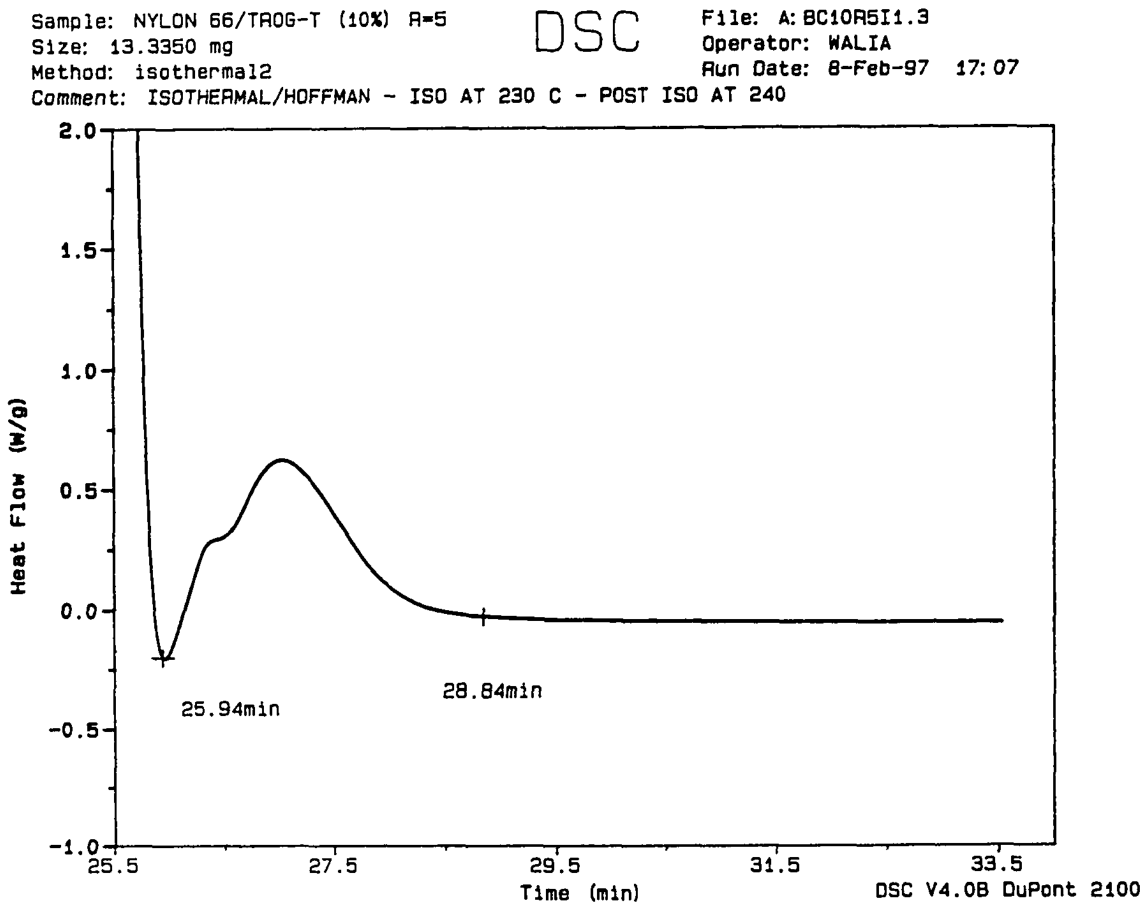


FIGURE C.22: Isothermal Run for 10% Nylon 6,6/Nylon 6,12, RT=5 min Blend, Unannealed (A=0) at 230°C

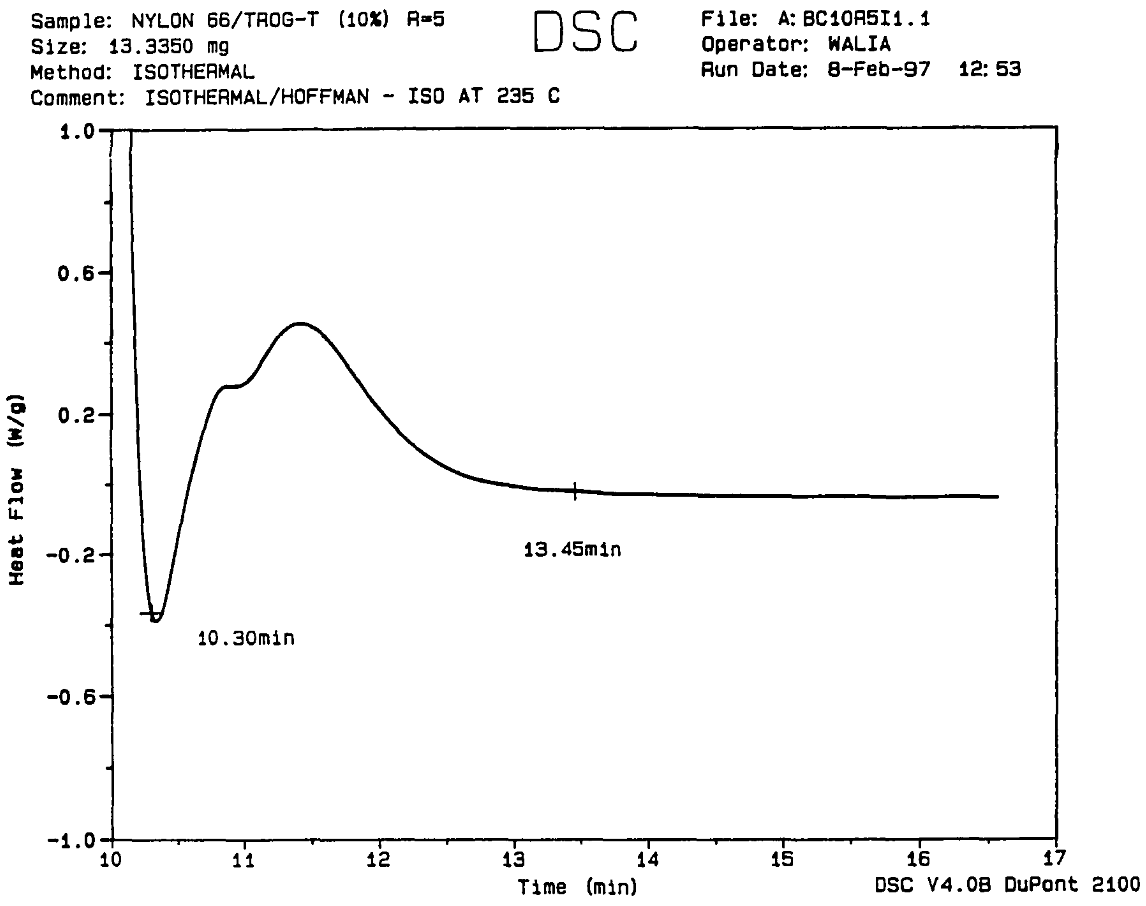


FIGURE C.23: Isothermal Run for 10% Nylon 6,6/Nylon 6,12, RT=5 min Blend, Unannealed (A=0) at 235°C

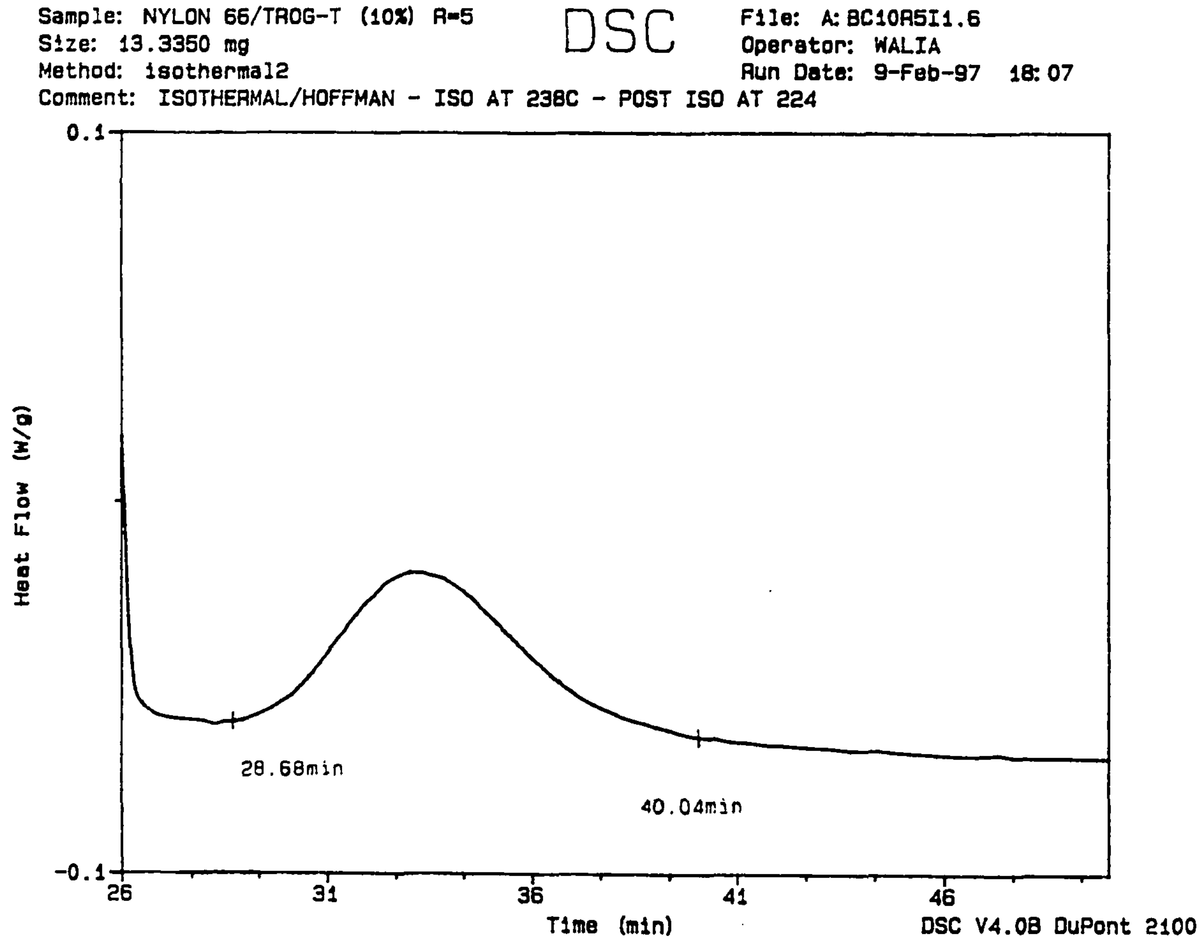


FIGURE C.24: Isothermal Run for 10% Nylon 6,6/Nylon 6,12, RT=5 min Blend, Unannealed (A=0) at 238°C

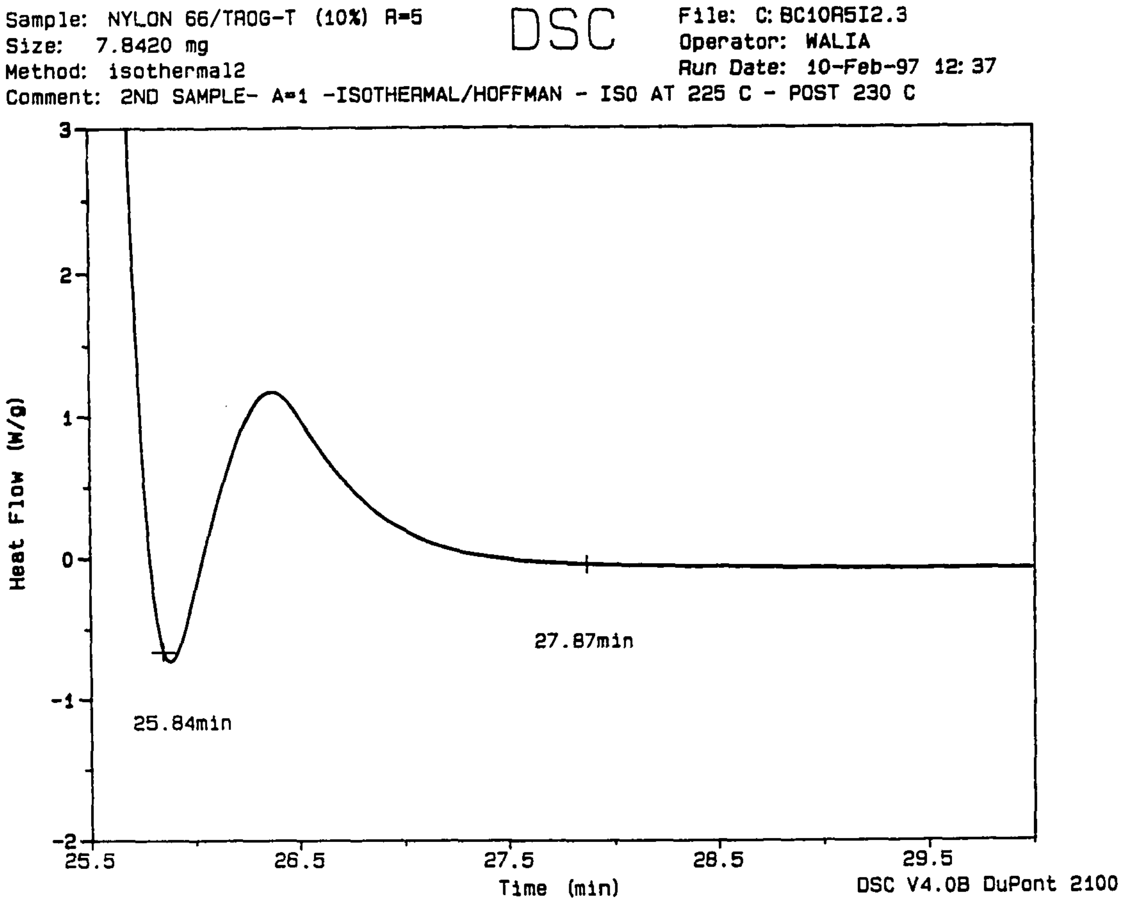
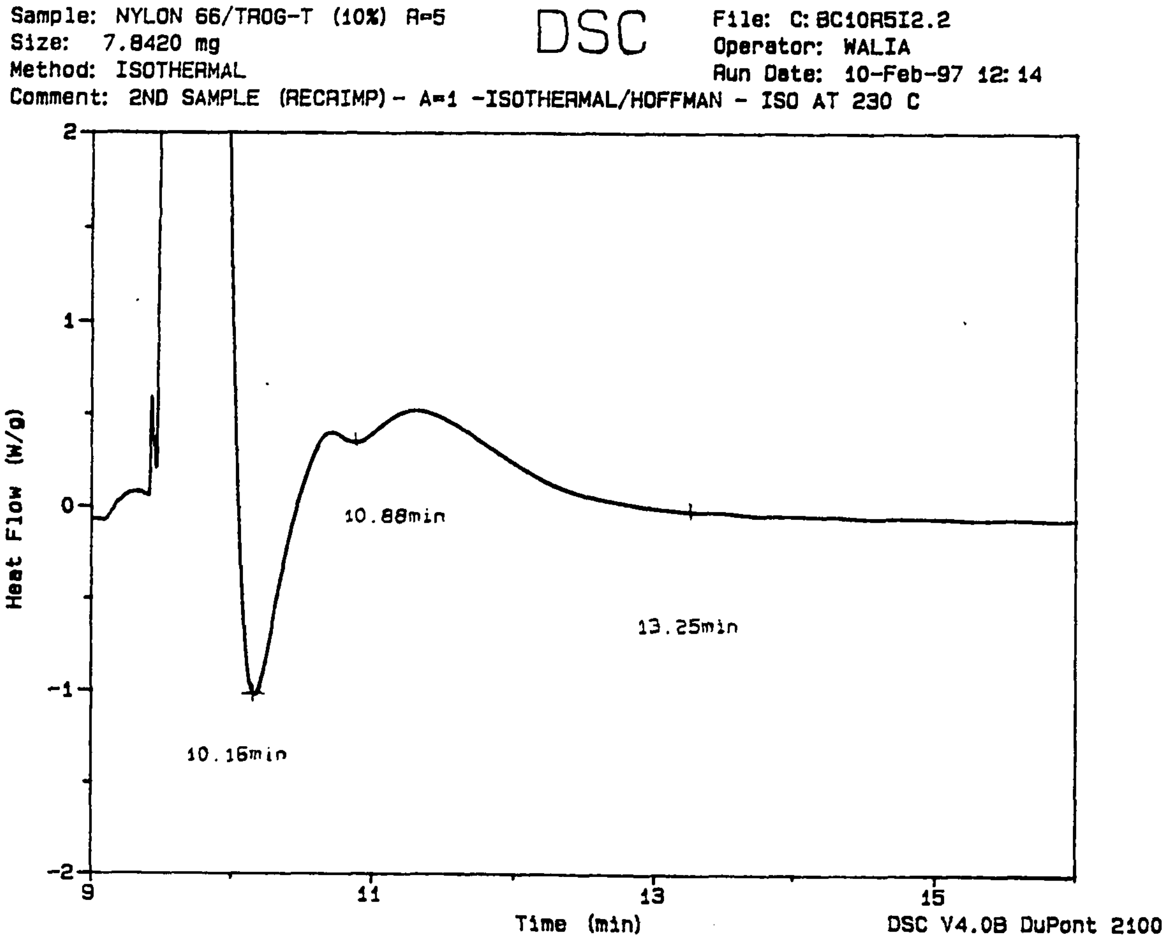


FIGURE C.25: Isothermal Run for 10% Nylon 6,6/Nylon 6,12, RT=5 min Blend, Annealed for 1 hr (A=1) at 225°C



Sample: NYLON 66/TROG-T (10%) R=5
Size: 7.8420 mg
Method: ISOTHERMAL
Comment: 2ND SAMPLE (RECRIMP) - A=1 -ISOTHERMAL/HOFFMAN - ISO AT 230 C

File: C:BC10R5I2.2
Operator: WALIA
Run Date: 10-Feb-97 12:14

FIGURE C.26: Isothermal Run for 10% Nylon 6,6/Nylon 6,12, RT=5 min Blend, Annealed for 1 hr (A=1) at 230°C

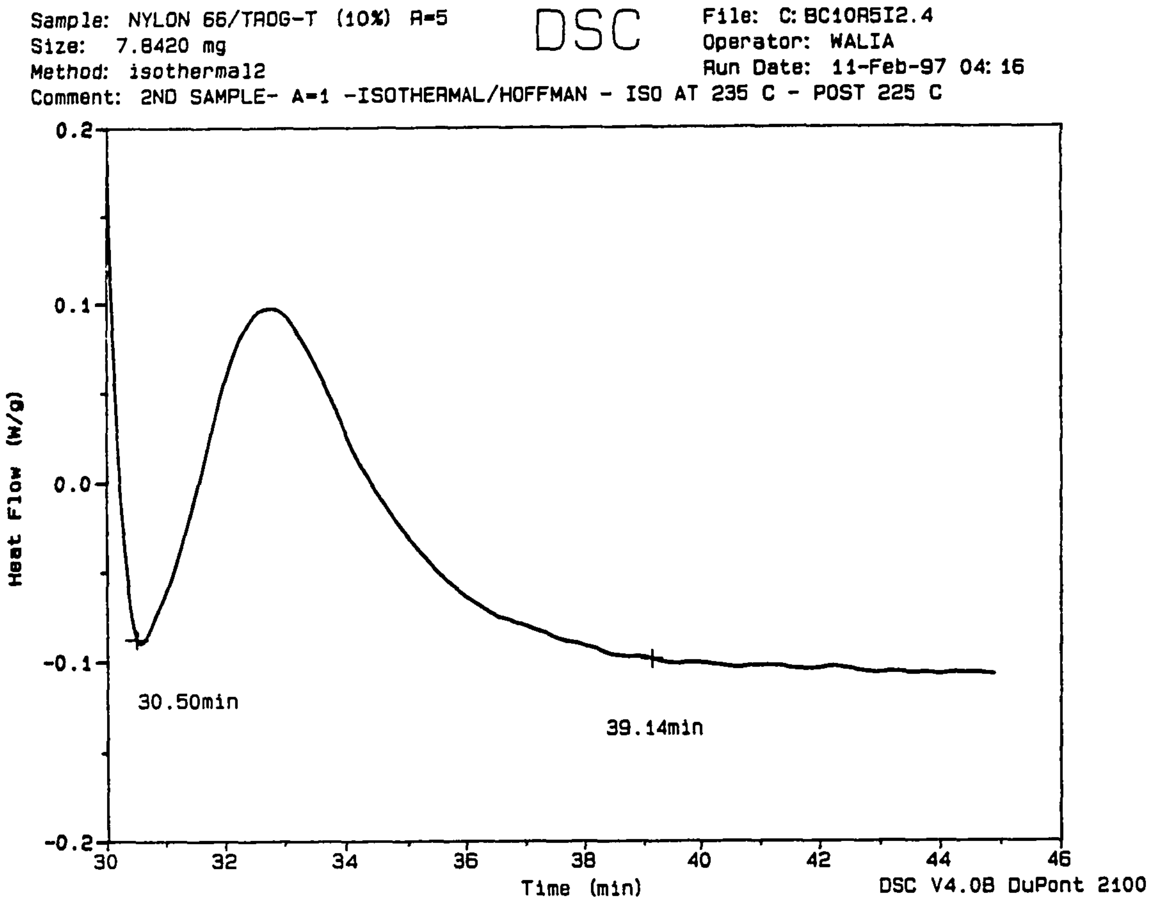


FIGURE C.27: Isothermal Run for 10% Nylon 6,6/Nylon 6,12, RT=5 min Blend, Annealed for 1 hr (A=1) at 235°C

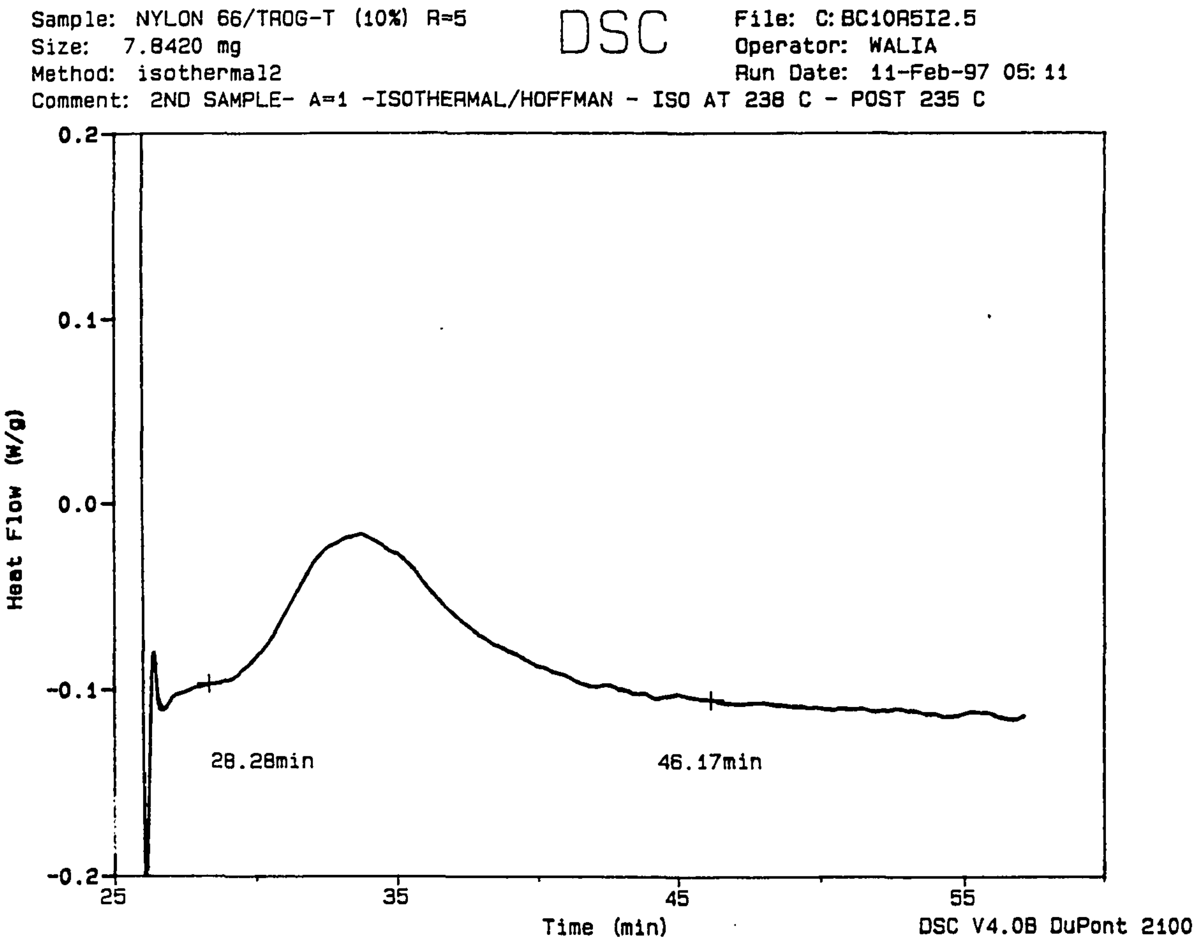


FIGURE C.28: Isothermal Run for 10% Nylon 6,6/Nylon 6,12, RT=5 min Blend, Annealed for 1 hr (A=1) at 238°C

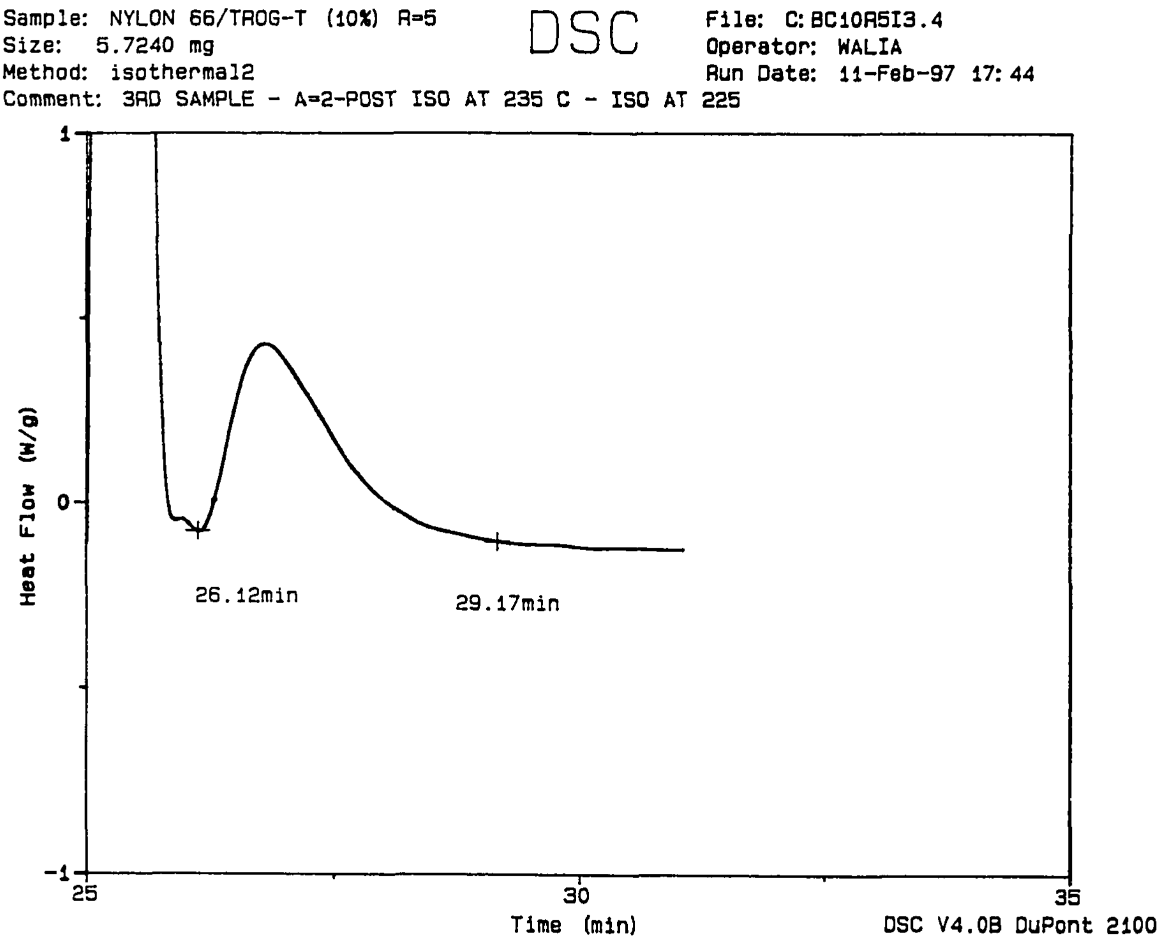


FIGURE C.29: Isothermal Run for 10% Nylon 6,6/Nylon 6,12, RT=5 min Blend, Annealed for 2 hrs (A=2) at 225°C

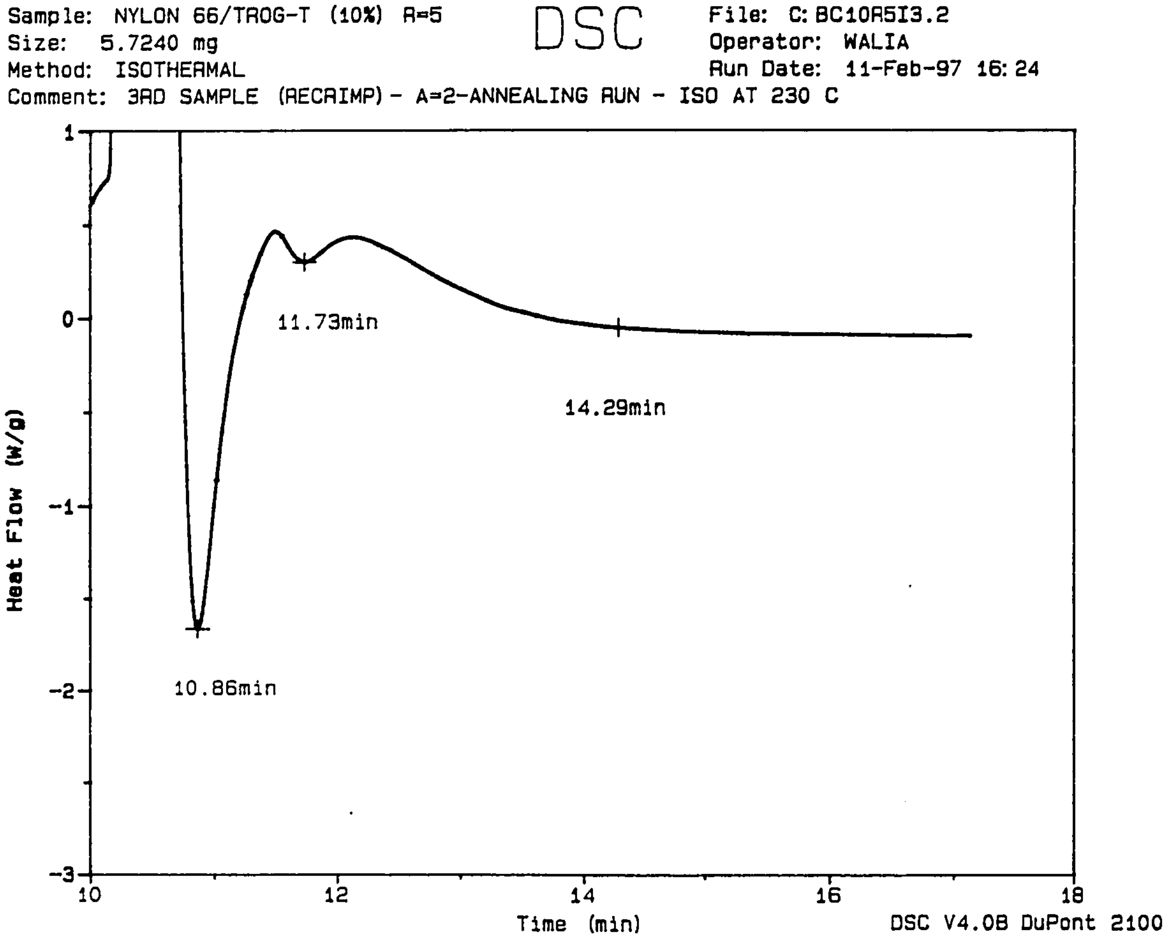


FIGURE C.30: Isothermal Run for 10% Nylon 6,6/Nylon 6,12, RT=5 min Blend, Annealed for 2 hrs (A=2) at 230°C

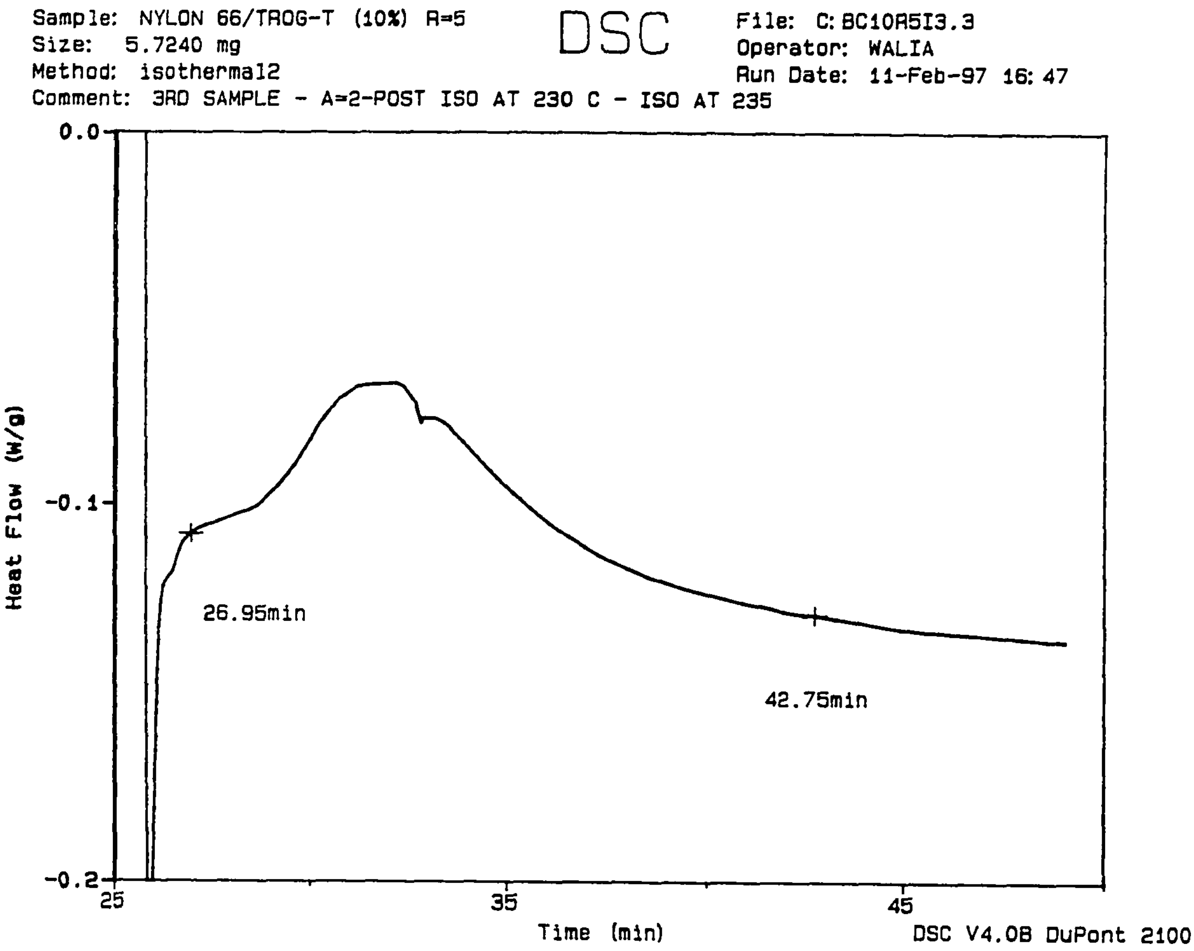


FIGURE C.31: Isothermal Run for 10% Nylon 6,6/Nylon 6,12, RT=5 min Blend, Annealed for 2 hrs (A=2) at 235°C

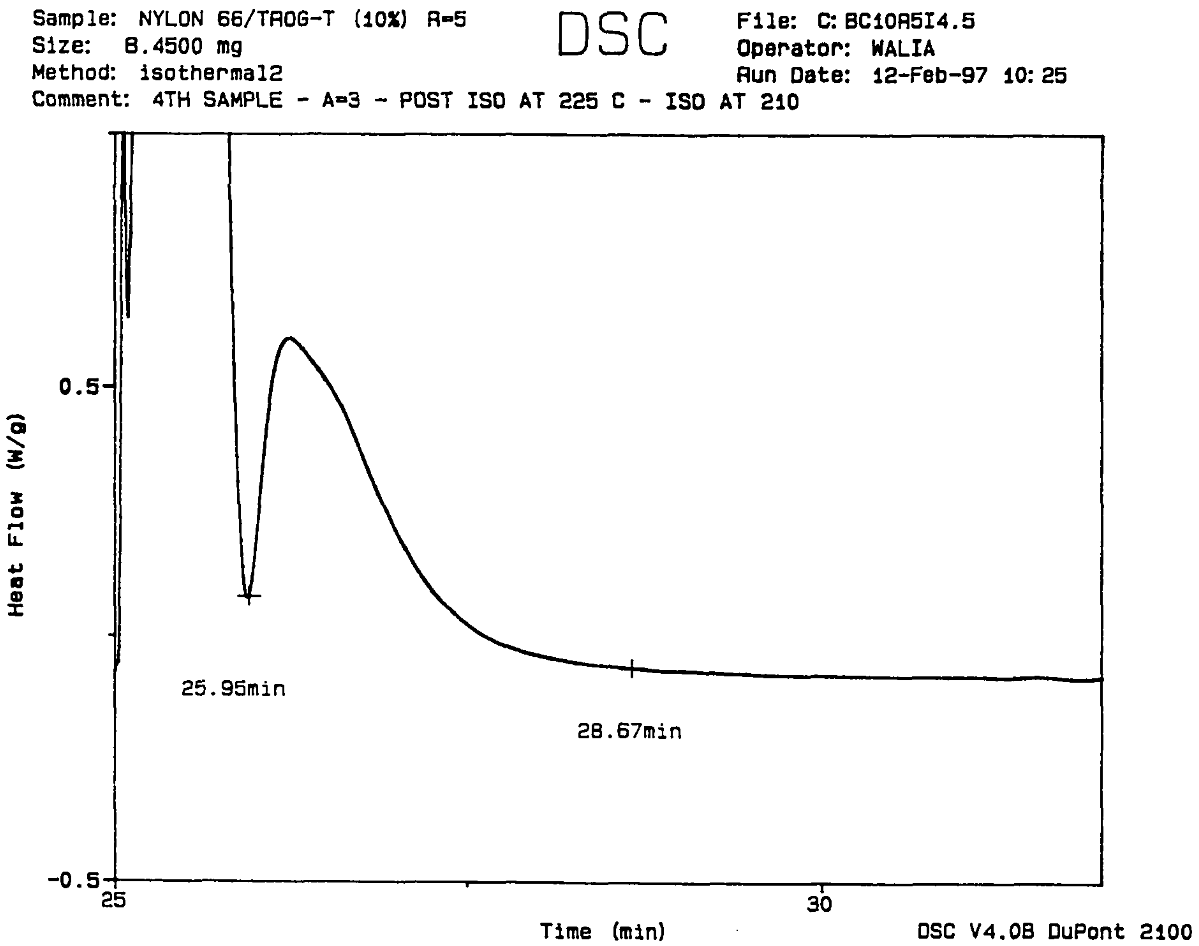


FIGURE C.32: Isothermal Run for 10% Nylon 6,6/Nylon 6,12, RT=5 min Blend, Annealed for 3 hrs (A=3) at 210°C

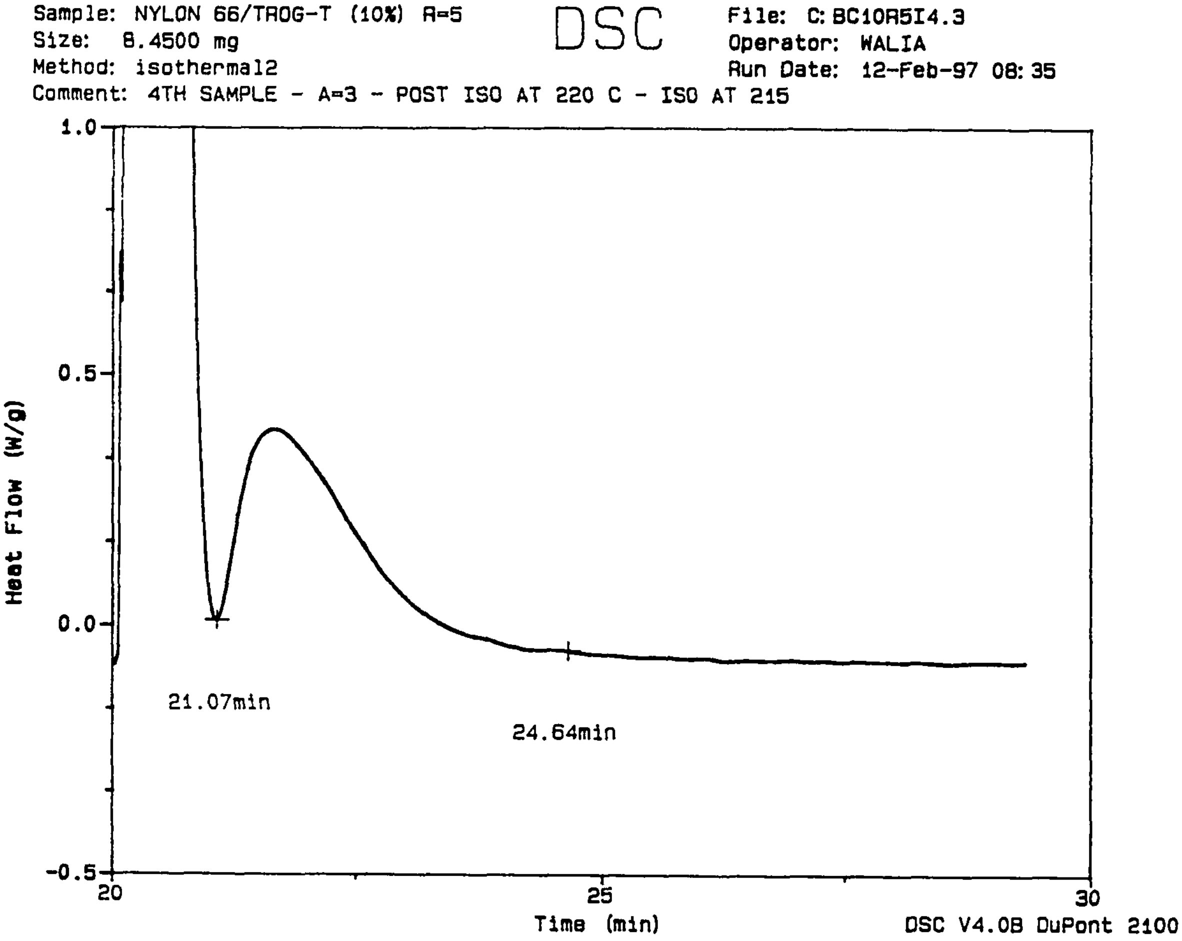


FIGURE C.33: Isothermal Run for 10% Nylon 6,6/Nylon 6,12, RT=5 min Blend, Annealed for 3 hrs (A=3) at 215°C

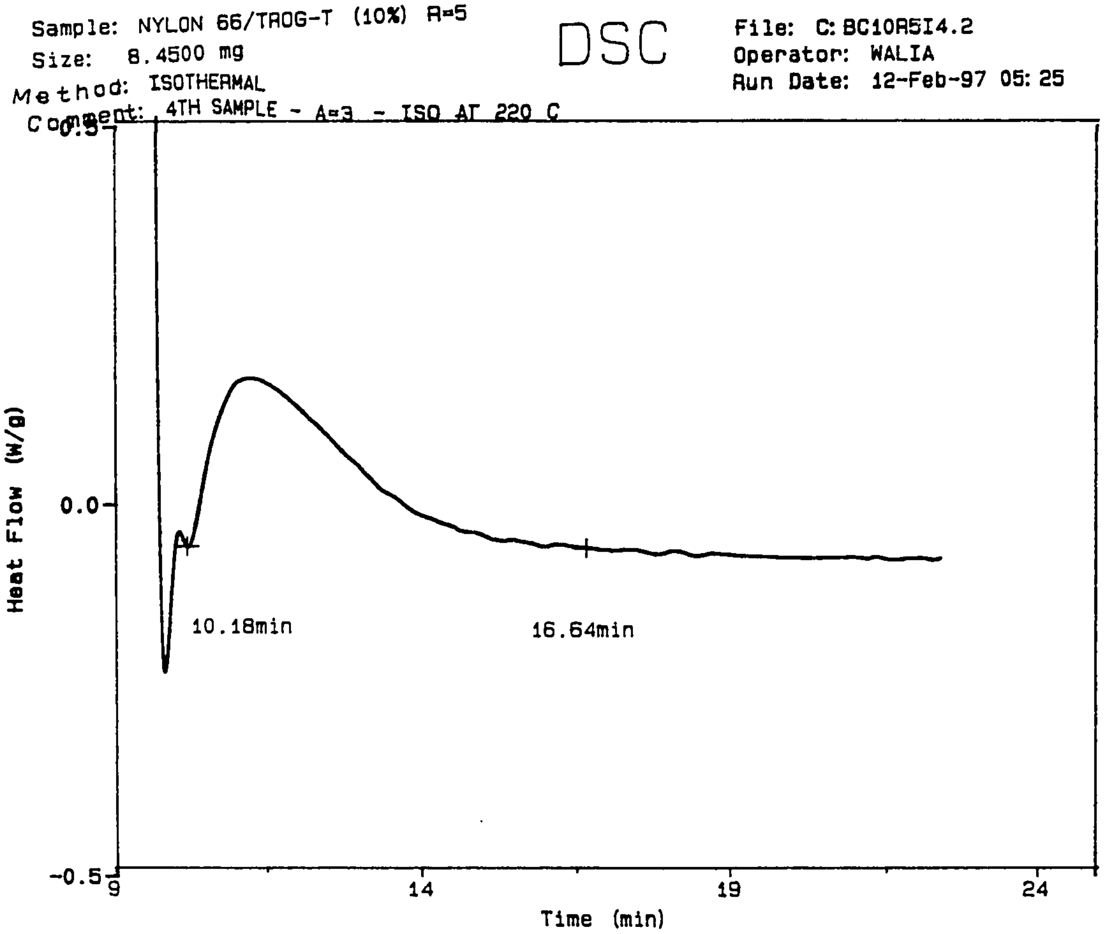


FIGURE C.34: Isothermal Run for 10% Nylon 6,6/Nylon 6,12, RT=5 min Blend, Annealed for 3 hrs (A=3) at 220°C

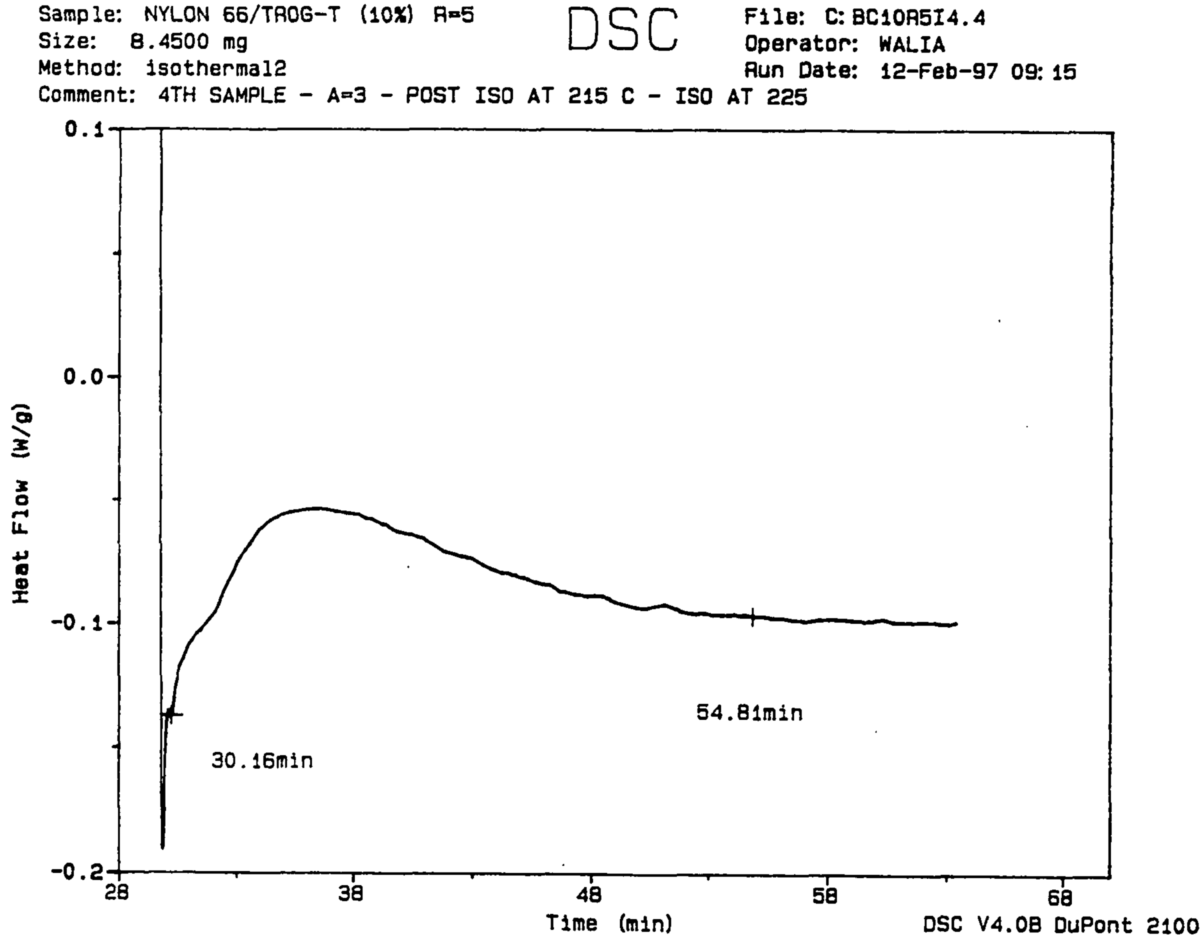


FIGURE C.35: Isothermal Run for 10% Nylon 6,6/Nylon 6,12, RT=5 min Blend, Annealed for 3 hrs (A=3) at 225°C

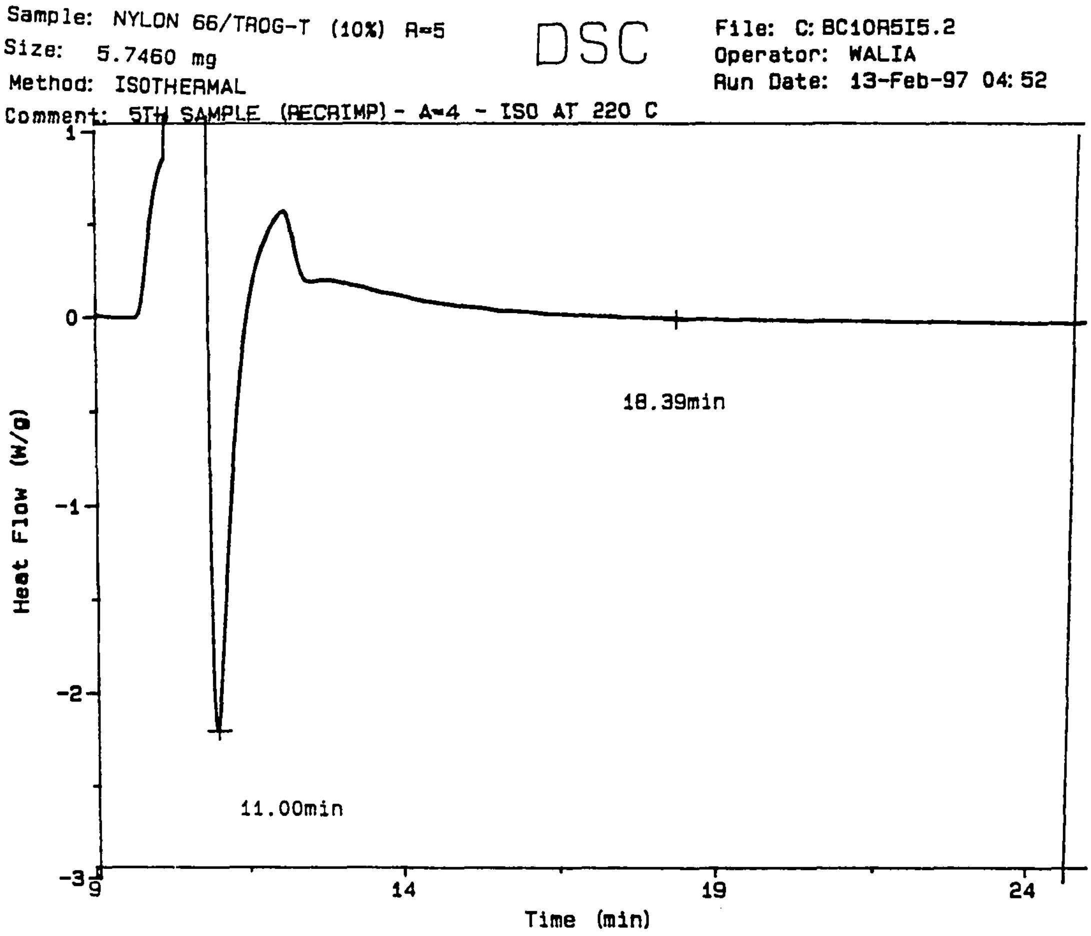
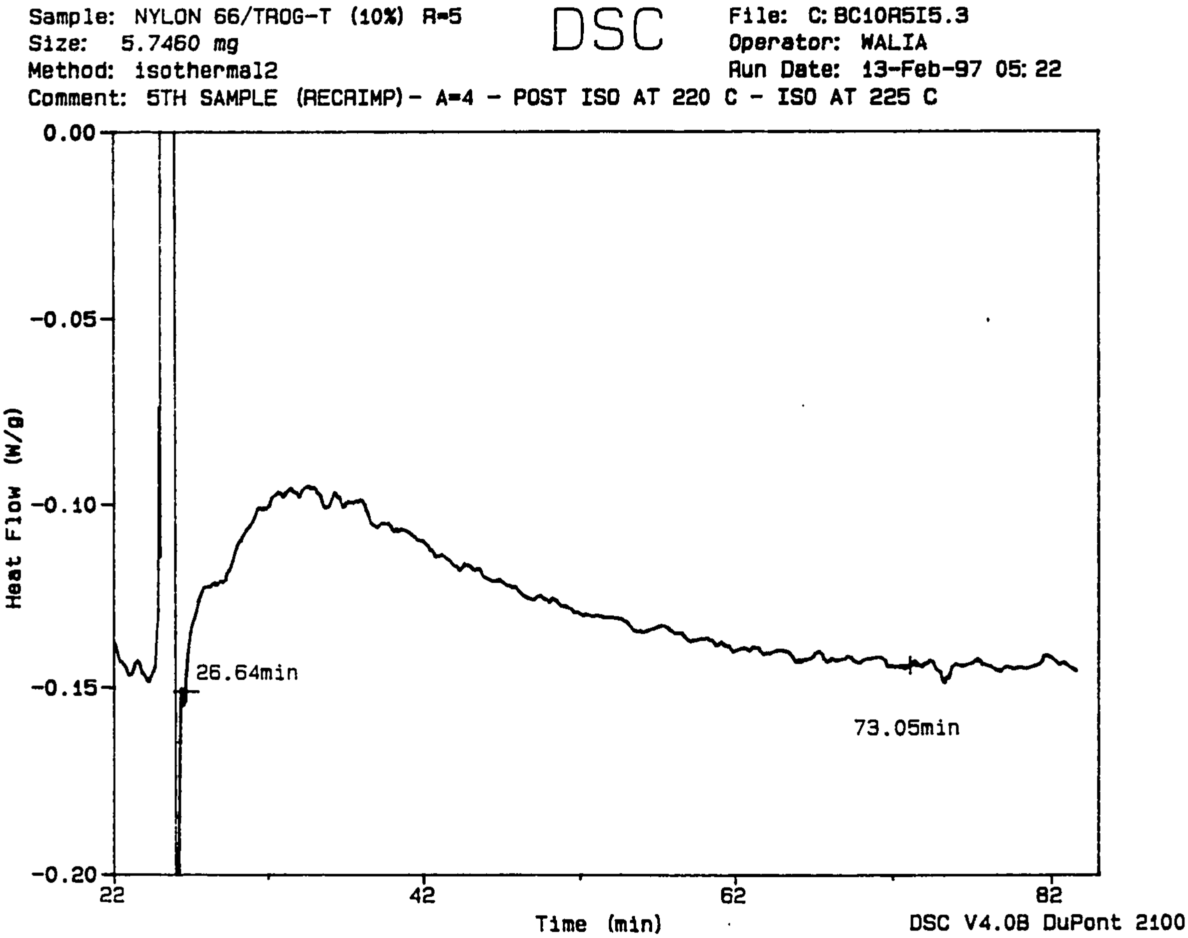


FIGURE C.36: Isothermal Run for 10% Nylon 6,6/Nylon 6,12, RT=5 min Blend, Annealed for 4 hrs (A=4) at 220°C



DSC

Sample: NYLON 66/TROG-T (10%) R=5
Size: 5.7460 mg
Method: isothermal2
Comment: 5TH SAMPLE (RECRIMP)- A=4 - POST ISO AT 220 C - ISO AT 225 C

File: C:BC10R5I5.3
Operator: WALIA
Run Date: 13-Feb-97 05:22

DSC V4.0B DuPont 2100

FIGURE C.37: Isothermal Run for 10% Nylon 6,6/Nylon 6,12, RT=5 min Blend, Annealed for 4 hrs (A=4) at 225°C

APPENDIX D

MISCIBILITY PREDICTIONS FROM ELLIS MODEL

Prediction of Miscibility: It is generally accepted that for two polymers to be miscible, a negative value of the Flory interaction parameter, χ_{12}, is indispensable. This is a direct implication of the requirement of an exothermic interaction. The Flory-Huggins lattice theory can be simply written as:

$$\frac{\Delta G_m}{RT} = \frac{\phi_1}{N_1}(\ln \phi_1) + \frac{\phi_2}{N_2}(\ln \phi_2) + \chi_{12}\phi_1\phi_2 \qquad \ldots(12)$$

This equation calculates the Gibbs free energy of mixing (ΔG_m) of two polymers having degree of polymerization N and volume fraction ϕ. For miscibility, $\Delta G_m < 0$ and this equation illustrates the importance of molecular weight and the interaction parameter χ_{12} in achieving that condition. Ellis [57,66,67,71-74] defined an effective interaction parameter χ_{blend}, as shown:

$$\chi_{12} \equiv \chi_{blend} = f[\chi_{12}] - \chi_{crit}; \text{ where } \chi_{crit} = (N_1^{-1/2} + N_2^{-1/2})^2/2 \qquad \ldots(13)$$

In the general case of high molecular weight polymers, χ_{crit} can be considered to be between 0.002-0.004 for $N_1 = N_2 \approx 500\text{-}1000$ and hence $\chi_{crit} \approx 0$. Then χ_{blend} is given as $\chi_{blend} = f[\chi_{12}]$. For a mixture of two polymers, defined as random copolymers A_xB_{1-x}/A_yC_{1-y}, this can be written as an algebraic sum of the intra- and intermolecular segmental interactions as shown below:

$$\chi_{blend} = (y - x)(1 - x)\chi_{AB} + (1 - y)(1 - x)\chi_{BC} + (x - y)(1 - y)\chi_{AC} \qquad \ldots(14)$$

This approach ignores any contribution from interaction of identical mers. Hence, by definition, for the case of polyamide blends, any contribution from amide-amide interactions is zero.

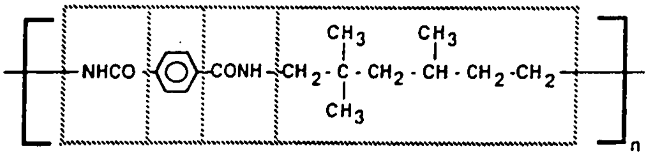
Model Development for Aliphatic-Aromatic Blends: Using the nomenclature of A, B and C representing methylene, amide and phenyl units, respectively, the aliphatic polyamides can be represented as A_xB_{1-x} and an aromatic polyamide of the type 3Me6T (Trogamid-T) can be represented as $A_yB_zC_{1-y-z}$. The structure and composition of 3Me6T are shown in Figure D.1. Applying the above interaction model to this blend system of copolymers $A_xB_{1-x}/A_yB_zC_{1-y-z}$, we get

$$\chi_{blend} = [(1 - x)(y - x) + z(x-y)]\chi_{AB} + (1 - y - z)(1 - x - z)\chi_{BC} + (1 - y - z)(x - y)\chi_{AC} \quad \ldots (15)$$

Ellis found that the blends of various aliphatic polyamides with 3Me6T showed a clear correlation between miscibility and the concentration of methylene units of the aliphatic polyamides. nylon 3Me6T was found to be soluble in nylons 6, 66, 69, 610, and 612 but insoluble in nylons 4, 46, 11, and 12. By synthesizing copolymers of caprolactam/2-pyrrolidinone and caprolactam/laurolactam, the critical limits, defining the transition from the miscible to the immiscible region, were determined. The limits were found to be x=0.76 and x=0.84. A copolymer with x=0.758 was found to exhibit only partial miscibility, while a copolymer with x=0.847 was found to exhibit critical behavior in the form of an LCST (lower critical solution temperature).

Knowing that $\chi_{blend}=0$ at x=0.76 and 0.85, two equations can be formulated. Assuming a value of $\chi_{blend}=-0.005$ for a nylon 6/nylon 3Me6T blend gives the necessary third simultaneous equation to solve for the three unknowns - χ_{AB}, χ_{BC}, and χ_{AC}. The assumed value of χ_{blend} only affects the overall scaling of the model and not the miscibility boundary. Figure D.2 [67] shows χ_{blend} values of 3Me6T/aliphatic polyamide blends versus the methylene content (x) of the aliphatic polyamide. Figure D.2 also shows the calculated behavior of nylon 6IcoT (Zytel 330) blends with aliphatic polyamides. Nylon 6,6 is predicted to be completely miscible with this amorphous nylon and this has been observed experimentally [66,67]. DMTA runs on the nylon 6,6/Zytel 330 blends prepared on the Maxwell extruder were observed to be miscible. In fact χ_{blend} value of nylon 6IcoT/nylon 6,6 blend would be higher (more negative) than nylon 3Me6T/nylon 6,6 blend, indicating higher miscibility.

NYLON 3Me6T



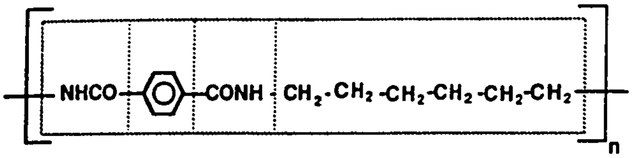
MER VOLUME FRACTION

METHYLENE y	AMIDE z	PHENYL* l-y-z
0.5723	0.1915	0.2362

*100% 1,4 - ISOMER

Structure and composition of nylon 3Me6T.

NYLON 6IcoT



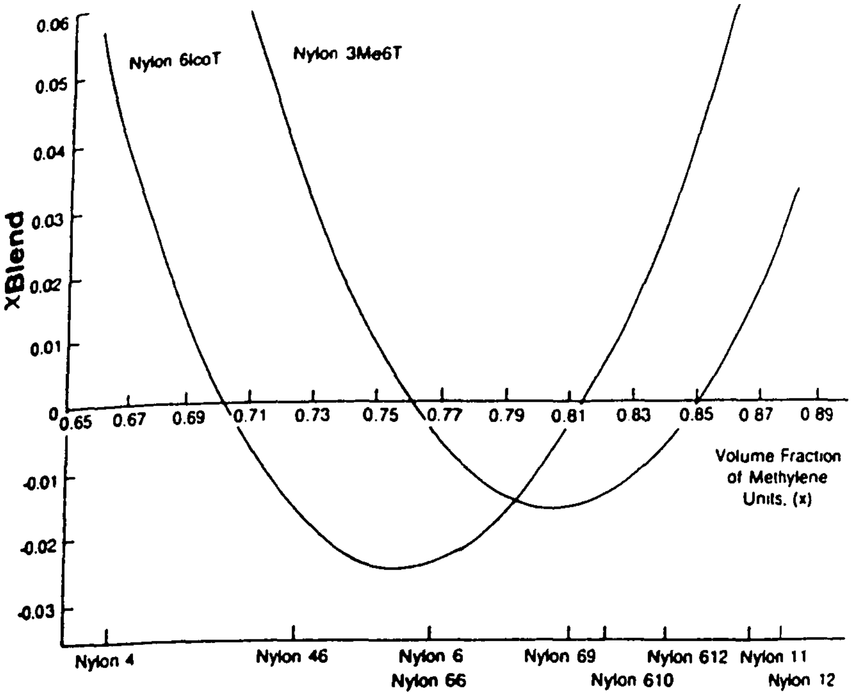
MER VOLUME FRACTION

METHYLENE y	AMIDE z	PHENYL* l-y-z
0.4702	0.2373	0.2925

*mixture of 1,4- and 1,3 -isomers 1:2

Structure and composition of nylon 6IcoT.

Figure D.1: Structure and composition of Trogamid-T (3Me6T) and Zytel 330 (nylon 6IcoT)



Calculated values of χ_{blend} of aromatic polyamide/ aliphatic polyamide blends.

Figure D.2: χ_{blend} values of 3Me6T and nylon 6IcoT with aliphatic polyamide blends versus the methylene content (x) of the aliphatic polyamide

INFLUENCE OF POLYMERIC ADDITIVES ON THE MELTING AND CRYSTALLIZATION BEHAVIOR OF NYLON 6,6

By

Parvinder Walia

A DISSERTATION

Submitted to
West Virginia University
In partial fulfillment of the requirements for
the Degree of
Doctor of Philosophy

APPROVAL OF EXAMINING COMMITTEE

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John Zondlo, Ph.D.

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Peter Stansberry, Ph.D.

Gangarao Hota, Ph.D.

Ben Dawson-Andoh, Ph.D.

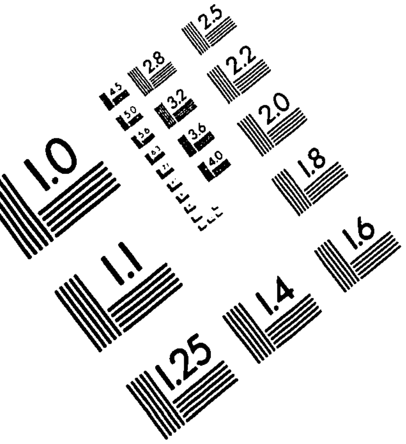
04/27/98

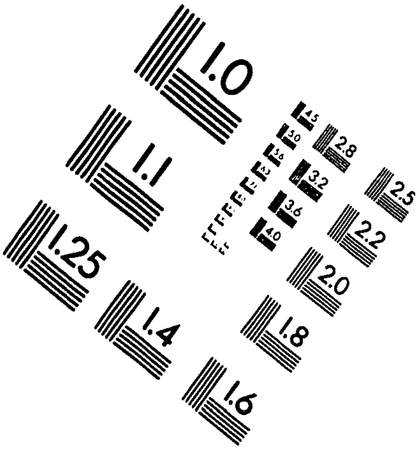
Date

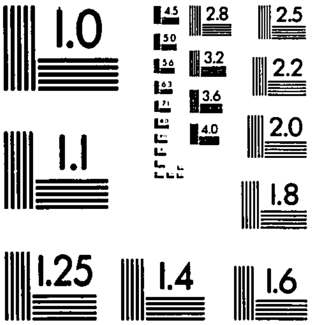
Rakesh Gupta

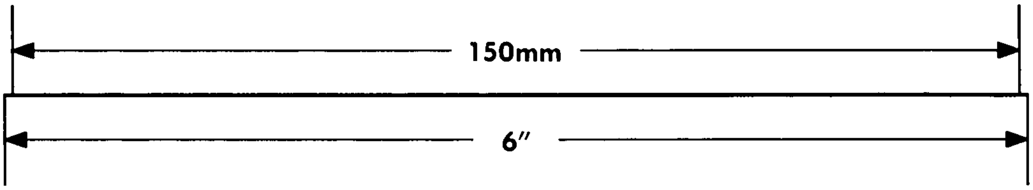
Rakesh Gupta, Ph.D., Chair

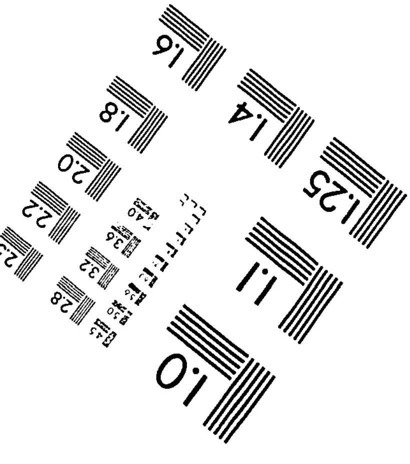
IMAGE EVALUATION
TEST TARGET (QA-3)

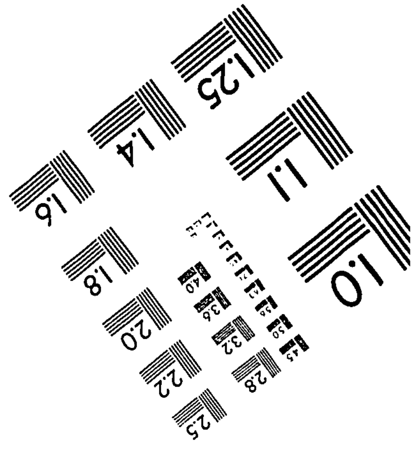












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