

Miscibility in blends of aliphatic polyamides and an aromatic polyamide, nylon 3Me6T

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Calorimetric and morphological investigations of blends of nylon 6 containing an amorphous aromatic polyamide, nylon 3Me6T, have shown them to be miscible across the entire range of composition. Amorphous blends illustrate the familiar monotonic and concave dependence of T_g upon composition which correlates well with existing theory. Crystallization of the nylon 6 component has been found to occur upon annealing, which is also accompanied by an unusual broadening of the glass transition in blends in the middle of the composition range. This phenomenon has been ascribed to a morphologically imposed heterogeneous distribution of the amorphous polyamide in the resultant mixed amorphous phase. Optical transmission microscopy has revealed a continuous spherulitic texture within the crystallized blends which confirms the absence of any critical solution behaviour. Preliminary investigations of the solution behaviour of nylon 3Me6T in nylons 4, 46, 66, 69, 610, 612, 11 and 12, respectively, indicate a correlation between miscibility and the relative abundance of amide functionalities of the latter. It is proposed that the behaviour observed is amenable to interpretations based upon a mean-field binary interaction model.

(Keywords: blends; polyamides; miscibility; glass transition; morphology; binary interaction model)

INTRODUCTION

The continued attraction of investigating polymer blends is justified from both a practical interest, as a simple method of formulating new materials with tailored properties, and a fundamental pursuit to elucidate more fully the factors controlling phase behaviour of polymer blends in general. With reference to the latter, the thermodynamic arguments that define polymer-polymer solution behaviour are by now well known^{1,2}. An inescapable difficulty remains, however, in the ability to measure exactly their relative contribution to the Gibbs free energy of mixing. Therefore, the ability to predict the outcome of mixing two high polymers remains a nascent science. The virtually zero contribution of the combinatorial entropy to the free-energy balance had in the recent past led to a widely accepted belief that the condition of thermodynamic miscibility would be a relatively rare occurrence. However, an ever-increasing list of miscible polymer pairs has indicated that the overall exothermic interaction necessary to achieve this state occurs with a greater frequency than was generally anticipated. These discoveries, coupled with recent advances of theory³⁻⁵, have focused attention on the chemical species and their resulting interactions within polymer structures as determinants of polymer-polymer solution behaviour. It is with this background that the work described here was undertaken.

This paper expands on a previous announcement⁶ of the observed miscibility of an aliphatic polyamide, nylon 6, and an amorphous aromatic polyamide, denoted as nylon 3Me6T. In addition to this, the solution behaviour of the aromatic polyamide in a homologous series of aliphatic polyamides, nylons 4, 46, 66, 69, 610, 612, 11 and 12, respectively, will also be described briefly. Recent

studies⁷⁻¹⁰ involving binary blends of mainly aliphatic polyamides have been small in number and generally inconclusive with regard to formulating any structure-property correlations that may exist between them. However, the collected evidence available would tend to suggest that immiscibility is the dominant phase behaviour within these systems. It should also be noted that the number of miscible amorphous/semicrystalline polymer blends is quite low in relation to the number of binary amorphous blends¹. Interestingly, this paper cites for the first time a number of examples of the former category whose components are readily available from commercial sources. This fact gains additional significance when considering the importance of these materials as a class of engineering polymers which are used extensively in a large number of applications.

EXPERIMENTAL

Materials

The principal polymers used in this study are nylon 3Me6T (Trogamid T), a condensation product of dimethyl terephthalate and 2,2,4-trimethyl-1,6-hexanediamine (Dynamit Nobel), and Zytel 211, a general-purpose unextracted nylon 6 (DuPont). Additional polymers incorporated into the study include nylon 4 (Chevron Research); nylon 46 (Allied-Signal); Zytel 101, a general-purpose nylon 66; nylon 69 (Aldrich Chemical); nylon 610 (Aldrich Chemical); Zytel 151, a general-purpose nylon 612; Rilsan AESNO, a standard unmodified extrusion grade; nylon 12 (Rilsan Corp.) and Rilsan BESNO, a nylon 11 of similar nature to Rilsan AESNO. The structural formulae of nylon 6 and nylon 3Me6T are shown in *Table 1*.

Table 1 Structure and properties of nylon 6 and nylon 3Me6T

Material	Structure	T_g onset (°C) (K)	T_g midpoint (°C) (K)	Incremental change in heat capacity at T_g , ΔC_p (J g ⁻¹ K ⁻¹)
Nylon 6 (Zytel 211)	$\left[\text{-(CH}_2\text{)}_5\text{-}\overset{\text{O}}{\parallel}\text{-C-N-} \right]_n$	42 (315)	45 (318)	0.827 ^a
Nylon 3Me6T (Trogamid T)	$\left[\text{-N-}\overset{\text{O}}{\parallel}\text{-C-}\langle\text{C}_6\text{H}_4\rangle\text{-}\overset{\text{O}}{\parallel}\text{-C-N-CH}_2\text{-C(Me)}_2\text{-CH}_2\text{-CH(Me)-CH}_2\text{-CH}_2\text{-} \right]_n$	147 (420)	150 (423)	0.39 ^b

^a Ref. 16^b Ref. 12

Although the structure shown for nylon 3Me6T has been idealized as the 2,2,4-trimethyl derivative, high-resolution n.m.r. spectroscopy has revealed the presence of a number of isomers. Nevertheless, the ratio of aromatic to aliphatic protons was found to be in agreement with the structure given. N.m.r. also confirmed the presence of only the 1,4-substituted phenyl component, with negligible quantities of the 1,3-substituted derivative.

Blend preparation

Blends of nylon 3Me6T and nylon 6 were prepared with nylon 3Me6T contents of approximately 11, 22, 30, 40, 49, 60, 73, 80 and 90% by weight, respectively, in the following manner. After drying in a vacuum oven at 120°C for 18 h the pre-weighed blends, approximately 3 g total mass, were dissolved in 98% formic acid to provide an approximate 2–3% by weight solution. The clear solutions were precipitated by dropwise addition into an excess (21) of vigorously stirred deionized water. The precipitates were washed exhaustively in deionized water, filtered and dried in a vacuum oven for 18 h, at ambient conditions. After further drying at 110°C for 18 h, the blends were compression moulded into thin films, approximately 1 mm in thickness, at a temperature of 260°C. These films were dried in an Abderhalden-type drying apparatus, under vacuum, in the presence of phosphorus pentoxide using refluxing xylene as the heating medium (b.p. \approx 140°C). Samples were stored over anhydrous calcium chloride.

Single blends of nylon 3Me6T with nylon 66 and 612, respectively, were prepared with contents of 50% by weight using an identical procedure. Similar blends were prepared using nylons 11 and 12 using a 4:1 trifluoroethanol/chloroform mixture as the solvent¹¹ and methanol as the precipitating medium. Subsequent studies have indicated a solvent system based on trifluoroethanol and methylene chloride¹¹ to be a versatile medium for all polyamide blend preparations. Similarly, the use of diethyl ether as a precipitant produced a polyamide solvent/precipitate system which was much superior to the formic acid/water system. The latter method was used to prepare blends of nylon 3Me6T containing nylons 4, 46, 69 and 610, respectively. The blends obtained by either method did not yield any detectable differences. All of the pure polymers were subjected to an identical preparative route as that used for their blends in order to provide a uniform point of reference. An additional nylon 6 blend, containing

approximately 47% by weight nylon 3Me6T, was prepared by melt blending the unprocessed materials using a Brabender Plasticorder equipped with a mixing chamber. Mixing was effected at a temperature of approximately 260°C, at high speed (200 r.p.m.), for 3 min.

Analytical procedures

Thermal analysis was conducted using a Perkin–Elmer Model 7 Series differential scanning calorimeter (d.s.c.) or a DuPont 1090 Thermal Analyzer equipped with a d.s.c. cell at a heating rate of 10°C min⁻¹. Values of the glass transition temperature T_g are reported both as the onset and the midpoint of the transition and values of T_m are reported as the maximum of the melting endotherm. Quantitative enthalpy changes were computed based on a calibration provided by the heat of fusion of an indium standard.

Morphology characterization was effected by optical transmission microscopy using a Leitz optical microscope equipped with crossed polarizers. Thin sections (approximately 1–2 μ m) of the compression-moulded polymers, annealed under the conditions described, were produced using a Reichert–Jung Polycut microtome.

Gel permeation chromatography (g.p.c.) was conducted on solutions of *m*-cresol at 110°C using a Waters Associates chromatograph. Molecular-weight averages were calculated based on a calibration provided by polystyrene standards. Both nylon 6 and nylon 3Me6T were of moderate molar mass with estimated values of $M_w \approx 12.0 \times 10^4$ and $M_n \approx 4.0 \times 10^4$, and $M_w \approx 6.3 \times 10^4$ and $M_n \approx 2.0 \times 10^4$, respectively. An M_n for nylon 6 of 2×10^4 is regarded as typical. Consequently the values obtained are somewhat high; however, in the absence of nylon standards, the values should be used for comparative purposes only.

A complete summary of the properties of the principal polymers is provided as Table 1. The value of the incremental change in heat capacity ΔC_p at T_g of the nylon 3Me6T material has been determined previously¹².

RESULTS AND DISCUSSION

Solution blending of polymers by coprecipitation from a common solvent is a rapid, convenient small-scale laboratory procedure which has a number of advantages over blending in the melt. It minimizes exposure to excessive thermal treatments, which in some instances can lead to chemical modification of the original

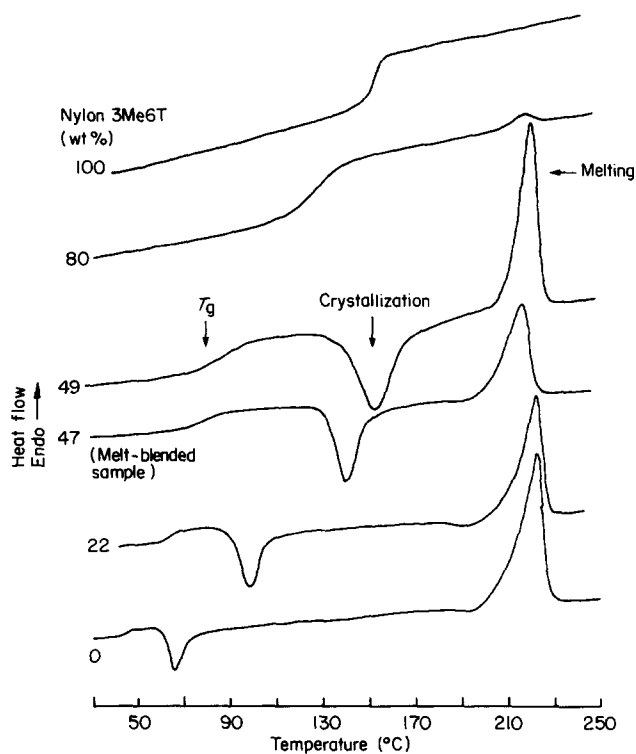


Figure 1 Representative thermograms of amorphous blends of nylon 6 and nylon 3Me6T, quench-cooled from the melt (260°C)

components, a condition that has been cited as a source of inconsistencies of observed phase behaviour¹³. Similarly, blends which display a critical miscibility point, e.g. a lower critical solution temperature (LCST), can be prepared in a state suitable for characterization. The blends prepared here were washed extensively and dried carefully under exacting conditions and a melt-blended sample was also prepared to provide a comparison with solution-blended samples.

Phase behaviour and thermal properties of amorphous blends

The mutual solubility of polymers in a binary blend is most conveniently assessed by thermal analysis, e.g. d.s.c., and in this respect the transitional behaviour usually provides strong evidence of the resulting phase behaviour. The occurrence of a single T_g , intermediate between those of the pure constituents, is often regarded as a criterion for complete miscibility. In cases where ambiguous discontinuities in specific heat are observed, secondary confirmation may be necessary. However, the blends described here were found to exhibit definitive transitions and secondary confirmation was considered to be unnecessary.

Preliminary results from the precipitated blends were consistent with the formation of a completely miscible blend, i.e. a single, sharp composition-dependent T_g , with the absence of a critical miscibility point in the temperature range of interest (40–300°C). Further detailed analysis was conducted on samples that had been compression moulded, as described previously. Qualitative inspection of the moulded films revealed tough coherent materials, optically clear at nylon 3Me6T contents greater than 30% by weight. Conversely, films containing a high nylon 6 content were opaque, a feature ascribed to the presence of spherulites.

Amorphous, or quench-cooled, samples were produced by heating a sample in a standard d.s.c. capsule, within the calorimeter, to a temperature of 260°C, which is above the melting point of nylon ($T_m \approx 220^\circ\text{C}$) and subsequently plunging the sample into liquid nitrogen. Representative thermograms of quench-cooled samples, shown in *Figure 1*, are clearly supportive of a single composition-dependent T_g and therefore the formation of a completely miscible blend. Although it is difficult to obtain completely amorphous nylon 6 by simple quench cooling, any resulting influence of crystallinity on T_g has been considered to be small and therefore insignificant. The transitional behaviour of the melt-blended sample, containing 47% by weight of nylon 3Me6T, was in accord with that obtained from the solution-blended materials (see *Figure 1*).

Couchman¹⁴ has provided a theoretical foundation for the prediction of the composition-dependent T_g in miscible polymer binary systems which has shown a precise ability to account for observed behaviour in a number of amorphous polymer blends¹⁵. Based on a classical thermodynamic interpretation of the glass transition phenomenon and utilizing the characteristic continuity of entropy through the transition, an expression has been derived, given here as equation (1), which allows for the calculation of the T_g of a polymer blend, T_{g12} , using the basic thermal properties of the pure constituents:

$$\ln T_{g12} = \frac{x_1 \Delta C_{p1} \ln T_{g1} + x_2 \Delta C_{p2} \ln T_{g2}}{x_1 \Delta C_{p1} + x_2 \Delta C_{p2}} \quad (1)$$

In this expression 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. Experimental determination of ΔC_p of amorphous nylon 6 is very imprecise owing to competing crystallization at the transition which obscures the true change in heat capacity. A further complication arises in that pure amorphous nylon 6 is difficult to form as some crystallization usually occurs during cooling prior to complete vitrification. However, an approximation determined by an extrapolation procedure is available¹⁶ and this value ($0.827 \text{ J g}^{-1} \text{ K}^{-1}$) is given in *Table 1* with the other values of the thermal properties of the pure components.

The agreement between experimental data and that predicted by equation (1) for the onset of T_g is excellent, as can be seen by inspection of *Figure 2*. The negative deviation of T_g with linear additivity can be reconciled with the mathematical nature of equation (1) viewed in conjunction with the empirical Simha-Boyer rule¹⁷: $\Delta C_p T_g \approx \text{const}$. Thus the lower T_g component usually possesses a larger ΔC_p which automatically imposes a concave dependence of T_g with composition in miscible polymer systems. Some exceptions have been observed^{18,19}, however; as a general rule a negative deviation from additivity should be expected.

The agreement between theory and the measured values of the onset T_g is unblemished. In contrast to this, the slight discrepancy between theory and the measured values for the midpoint can be reconciled to some extent by a midpoint value for pure nylon 6 which was almost certainly compromised by crystallization at the transition. It should be emphasized, however, that in a

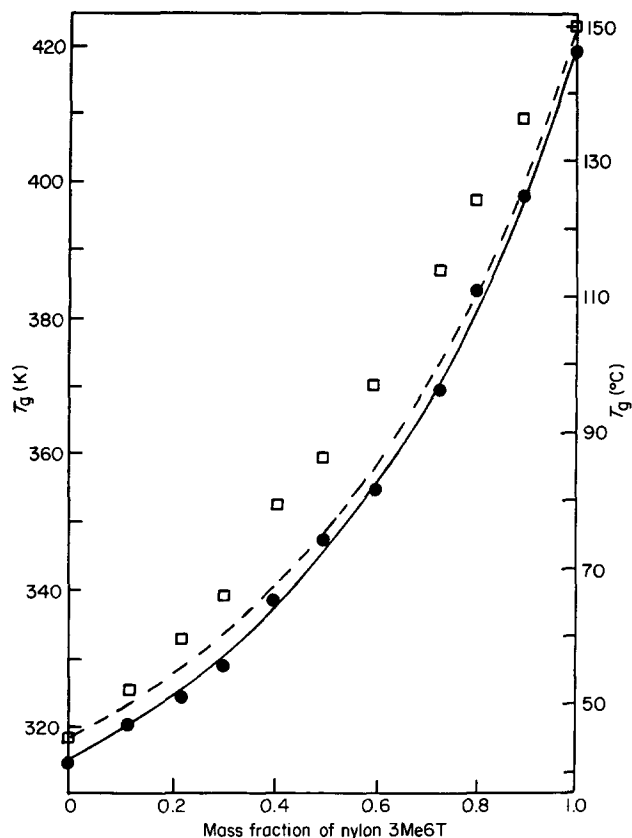


Figure 2 Glass transition behaviour of amorphous blends of nylon 6 and nylon 3Me6T: (●) onset T_g ; (□) midpoint T_g ; (—) onset T_g (equation (1)); (---) midpoint T_g (equation (1))

dynamic experimental determination of T_g by d.s.c. the onset will be most representative of the true transition. The midpoint measurement, however, does provide additional information with regard to the physical character of the transition. Although the transitional behaviour observed was relatively sharp, some broadening in the middle of the composition range could be detected, as illustrated in Figure 2. Transition width broadening is a recognized feature²⁰ of some miscible polymer blends within the middle section of the composition range. Attributable to microscopic concentration fluctuations, it is probably the principal contributor to the observed discrepancy between theory and experimental values of the midpoint T_g in the quenched amorphous blends.

Continued heating of the quench-cooled blends above their respective T_g induced crystallization of the nylon 6 component followed by eventual melting and the formation of a miscible blend in the melt. The magnitude and nature of these events are clearly composition-dependent, as can be seen in Figure 1. At a high nylon 3Me6T content (90% by weight), the time-scale of analysis is insufficient to allow any crystallization to occur, but, as will be described later, prolonged annealing above T_g does allow crystallization of the nylon 6 component even in the very dilute regime. It is worth noting that the melting behaviour of the nylon 6 in the blends, resulting from crystallization induced during the course of analysis, is not substantially different from that in the pure state.

Preliminary isothermal crystallization experiments, although not described here, have indicated that there is a substantial reduction in the overall rate of crystallization

of the nylon 6 in the blends. This is a natural consequence of the addition of a higher T_g amorphous additive to a low T_g semicrystalline polymer²¹. The nature of the crystallization exotherm of the amorphous blends, shown in Figure 1, is consistent with this behaviour. The maximum and width of the exotherm, when measured relative to the transition temperature of the blend, gradually increase compared to that obtained for nylon 6, providing a qualitative confirmation of a reduction of the rate of crystallization.

Phase behaviour and thermal properties of crystallized blends

Morphology. For a miscible polymer blend of an amorphous and semicrystalline polymer, where the amorphous polymer T_g is greater than that of the crystalline component and there is an LCST in the temperature range of interest, the phase diagram and hence phase behaviour can become extremely complex. Some of the relevant features of such a system have been elaborated upon recently within the literature²². An important consideration therefore was the confirmation of a liquid-to-solid transformation, i.e. crystallization, rather than a liquid-liquid phase separation, LCST, or a combination of both phenomena, as being responsible for the events described previously. The fact that the events illustrated in Figure 1 were quite reproducible on thermal cycling would tend to exclude the possibility of any critical behaviour, such as an LCST, occurring. Additional confirmation of this conclusion was provided by optical transmission microscopy of samples crystallized at 200°C.

Some examples of optical micrographs obtained on thin sections, using crossed polarizers, are shown in Figures 3a-e. All blends appear to have a continuous spherulitic morphology, although of different texture from that of nylon 6, supporting the absence of a liquid-liquid phase separation. The micrograph presented as Figure 3e shows nylon 6 crystallized in a very dilute blend (90% by weight nylon 3Me6T) and therefore it is difficult to see clearly the spherulitic morphology developed. The fibrillar, dendritic nature of the spherulites formed in the blends, even at a low nylon 3Me6T content, provides evidence of a considerable change of crystallization parameters from that normally observed for nylon 6. The nylon 6 morphology is representative of a high nucleation density followed by rapid radial growth of small spherulites leading to a random mosaic morphology of poorly defined spherulitic structure as shown in Figure 3a. In contrast to this, the blends crystallized under the same conditions have a more complete spherulitic structure indicative of a lower nucleation density. Evidence based on a number of studies of miscible crystalline/amorphous polymer blends²¹⁻²⁵ suggests that the parameters governing the rate of crystallization, radial spherulitic growth rate and hence the overall morphology of crystalline and amorphous domains will be very complex. Even qualitative conjecture is difficult since morphological features resulting from crystallization will depend upon time, temperature, composition and macromolecular diffusion in the liquid state. There are, however, some general trends to be expected for a miscible polymer system where a higher T_g amorphous component is added to a semicrystalline polymer. For example, there will be a narrowing of the crystallization

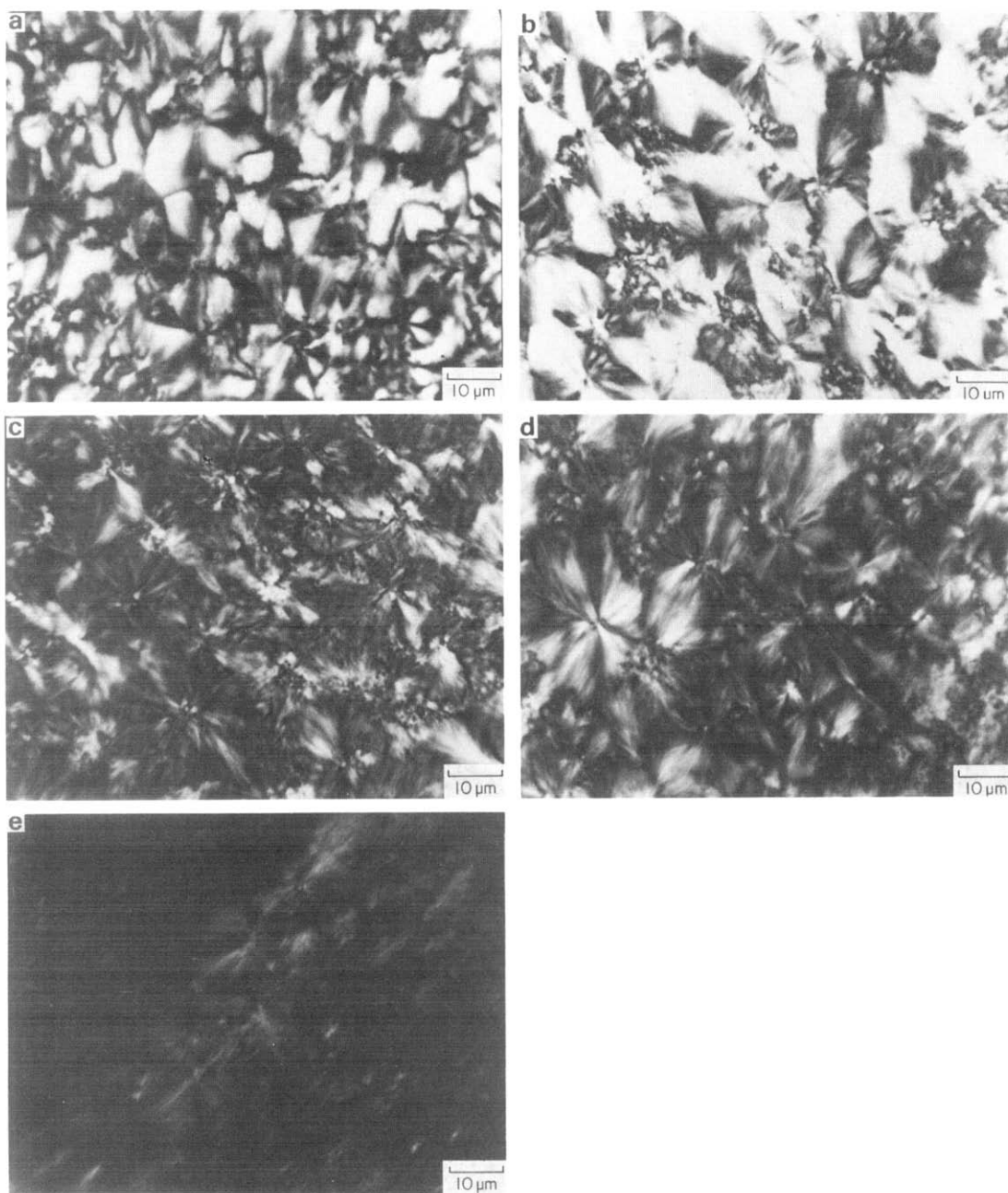


Figure 3 Optical micrographs of blends crystallized at 200°C: (a) nylon 6; (b) 11% w/w nylon 3Me6T; (c) 49% w/w nylon 3Me6T; (d) 80% w/w nylon 3Me6T; and (e) 90% w/w nylon 3Me6T

envelope (the temperature interval $T_g \rightarrow T_m$). Also one expects a reduction of the radial growth rate of spherulites manifested by a decrease of the overall rate of crystallization. The growth of spherulites in these types of blends involves the rejection of the non-crystallizable material from the growing crystal surface into the interlamellar regions. Thus it is possible to have two amorphous solutions in the crystallizing mass both in contact with each other and of different composition. There is obviously a thermodynamic driving force for homogenization but diffusion and hence kinetic factors play a vital role. This behaviour will contribute to the formation of dendritic spherulites, with a large spacing of the interlamellar regions similar to those observed here. Although no rigorous isothermal crystallization rate studies have yet been performed, it has been possible to detect that there is a reduction in the overall rate of

crystallization. The relevance of the phenomena discussed above to the morphology developed is self-evident. However, it is also probable that their influence on the thermal properties of the crystallized blends is equally important, as will be described subsequently.

Thermal studies. The bulk of the information presented here has been obtained by annealing blends for 18 h at crystallization temperatures T_c of 155, 170, 185 and 200°C, respectively. A time period of 18 h was selected to ensure the establishment of a morphological equilibrium, but it should not be considered to represent the minimum necessary to achieve this state. The formation of a homogeneous melt, prior to the commencement of annealing, was ensured by heating the blends to 265°C for 3 min. Samples produced in this way were characterized by d.s.c. immediately following the annealing process.

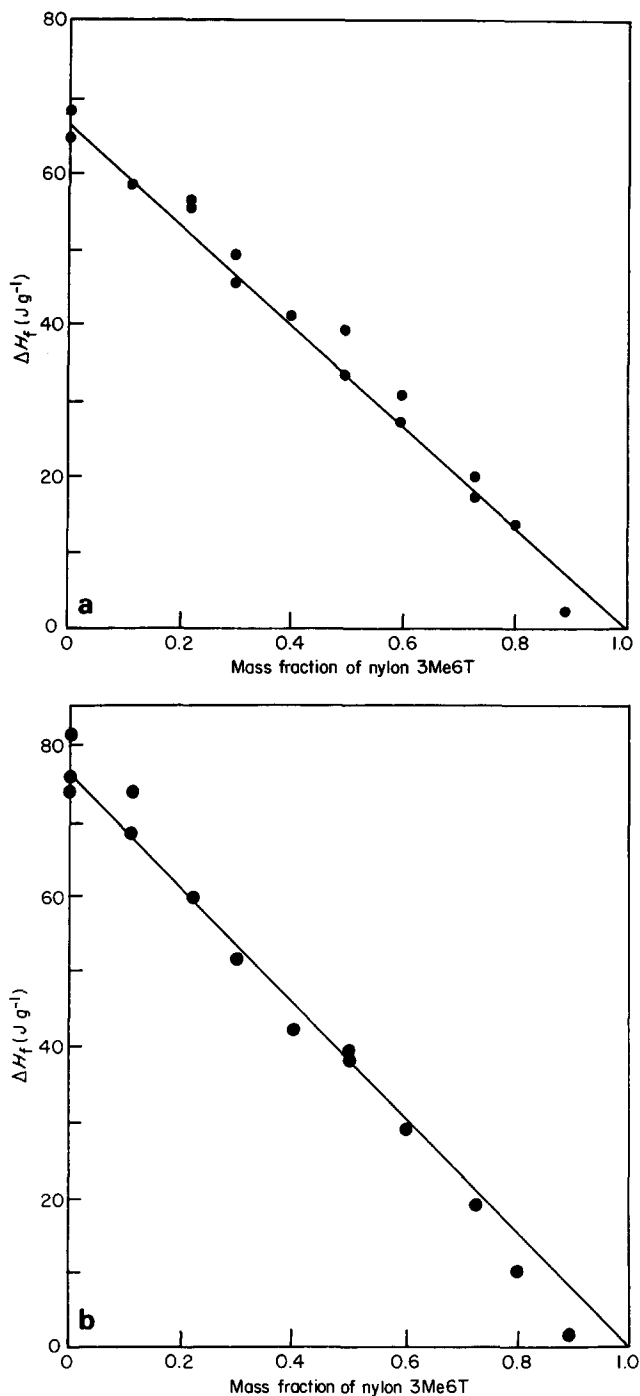


Figure 4 Heat of fusion ΔH_f of crystallized blends at (a) $T_c = 155^\circ\text{C}$ and (b) $T_c = 200^\circ\text{C}$: (—) linear additivity; (●) experimental data

Heat of fusion. Measurements of the heat of fusion ΔH_f as a function of blend composition are shown in Figures 4a and 4b together with the relationship defined by linear additivity. Similar results were obtained from blends annealed at 170 and 185°C, respectively. It should be noted that there is a slight variation of ΔH_f of pure nylon 6, obtained at different annealing temperatures. All of the blends were found to develop a crystalline nylon 6 phase upon annealing and except for blends containing in excess of 80% by weight nylon 3Me6T annealed at 200°C, the nylon 6 crystallized to the same extent as that in the pure state. This feature is in itself a little unusual in that although many miscible semicrystalline/amorphous polymer blends retain the ability of the semicrystalline

component to crystallize within the blend, this is usually absent or substantially diminished in the dilute regime. The results also appear to confirm the formation of a morphological equilibrium under these conditions; however, continued rearrangement during the course of thermal analysis can never be discounted. This becomes more significant when considering the measured T_m , as will be described subsequently, but it is probable that its influence on measured values of ΔH_f is minimal. The deviation from linear additivity of the blends with a high amorphous nylon content annealed at 200°C, as noted above, can be attributed to any one of several sources. The most plausible reason is the very slow rate of crystallization one can anticipate at this temperature in blends containing small quantities of nylon 6.

Melting behaviour and T_m . In general, the melting behaviour of nylon 6 is not significantly influenced by the presence of the miscible amorphous component when compared to that in the pure state. Inspection of Figure 5, showing a selection of representative thermograms, confirms this observation. The melting behaviour of nylon 6 has been studied extensively²⁶. However, all the data presented here pertain to that obtained from the sample subjected to the same procedures as those used for blend preparation. The multiple melting peaks observed

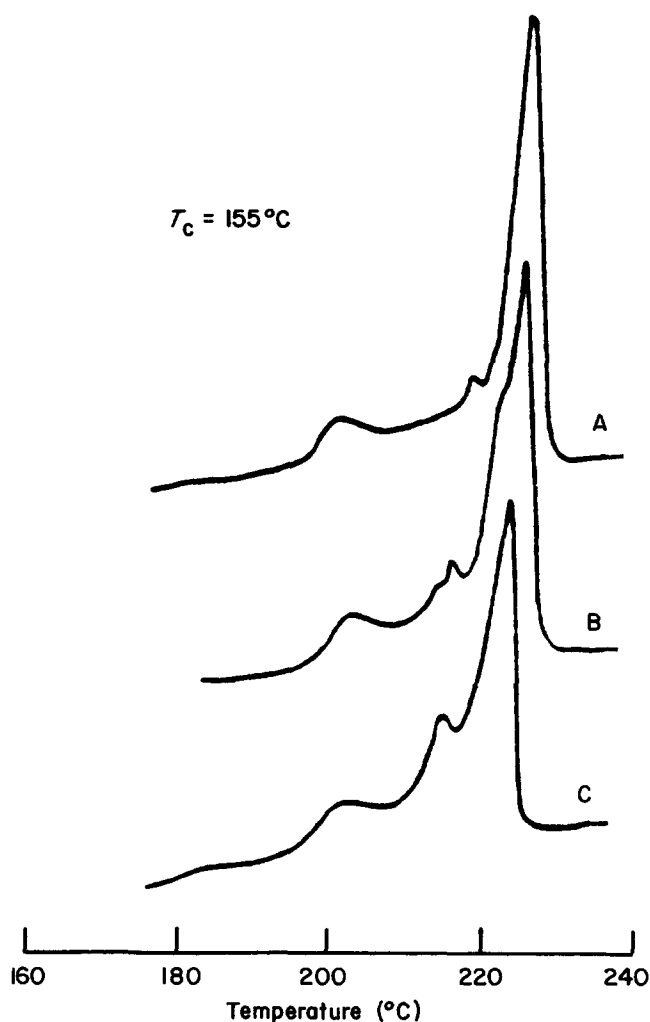


Figure 5 Representative thermograms of the melting behaviour of crystallized blends: A, nylon 6; B, nylon 6/30% nylon 3Me6T; C, nylon 6/49% nylon 3Me6T

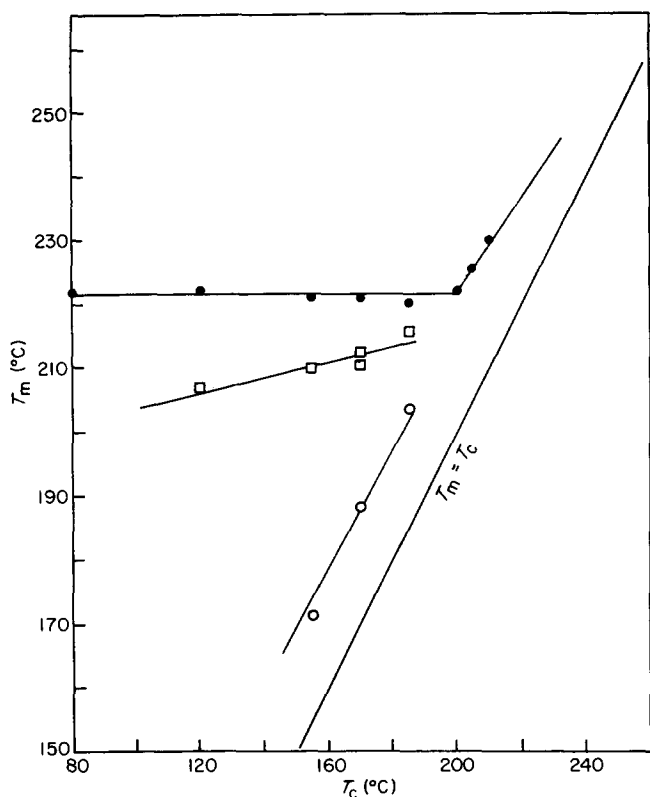


Figure 6 Melting behaviour of nylon 6: (●) principal melting endotherm; (□, ○) secondary melting endotherms

in nylon 6, annealed at temperatures below 200°C, are quite reproducible in the blends. Annealing at or above 200°C produces a single melting endotherm.

A quantitative summary of the melting behaviour of nylon 6, which includes some supplementary data obtained by annealing at different temperatures from those described previously, is shown in Figure 6. An important feature of the melting behaviour of pure nylon 6, as shown in Figure 6, is the relative insensitivity of the principal melting peak to annealing at a temperature below 200°C. This is in accord with previous work²⁷ and is symptomatic of crystalline rearrangement, such as lamellar thickening, during the course of thermal analysis. Therefore the value of T_m obtained from annealing below 200°C is not representative of the equilibrium state produced at the crystallization temperature in question. On annealing above 200°C, the rate of crystallization becomes extremely slow and above 210°C the rate is so slow that it was difficult to quantify the melting behaviour. The pre-melting endotherms shown in Figure 6 are associated with the melting of poorly developed crystalline structures and different crystalline forms²⁶.

The melting behaviour of blends containing 30% and 49% by weight of nylon 3Me6T are shown in Figures 7 and 8, respectively. In general, the melting behaviour of the nylon 6 component parallels that in the pure state. It is also possible to discern a slight depression of T_m ; however, in this instance it is not possible to assign this reduced T_m to either a kinetic or a thermodynamic effect.

The consequences of adding a miscible diluent, monomeric or polymeric to a crystalline polymer are well understood²⁸. A lowering of the chemical potential in the

amorphous phase results in a thermodynamic depression of the melting point and it is possible to utilize this phenomenon to estimate a value for the Flory interaction parameter, χ_{12} (ref. 29). There are a number of difficulties associated with this procedure, not the least of which is the small depression of T_m ($\approx 2-4^\circ\text{C}$) resulting from a usually small value of χ_{12} . Moreover the morphological influence on T_m is often of greater magnitude than the thermodynamic effect, and, although a Hoffman-Weeks approach²⁹ may be adopted to circumnavigate this obstacle, there are nonetheless many experimental drawbacks in applying this procedure^{21,30,31}.

For this particular system, equilibrium melting measurements would have to be conducted in a narrow range on blends annealed above 200°C where the rate of crystallization is extremely slow and there is always the potential of reduced thermal stability. In addition, extrapolation to an equilibrium T_m would have to be conducted over a considerable range of temperature. Despite these difficulties, studies are currently in progress to determine if a value of χ_{12} can be obtained by melting point depression experiments.

The glass transition. A summary of the transitional behaviour of the crystallized blends is presented in Figures 9 and 10 together with the data obtained from quench-cooled blends. The general features are similar for both annealing temperatures but there are some important differences when compared to those obtained from the amorphous samples.

The crystallization of the nylon 6 component involves the rejection of the non-crystallizable nylon 3Me6T into the liquid phase. As may be expected, this induces a compositional adjustment of the amorphous phase,

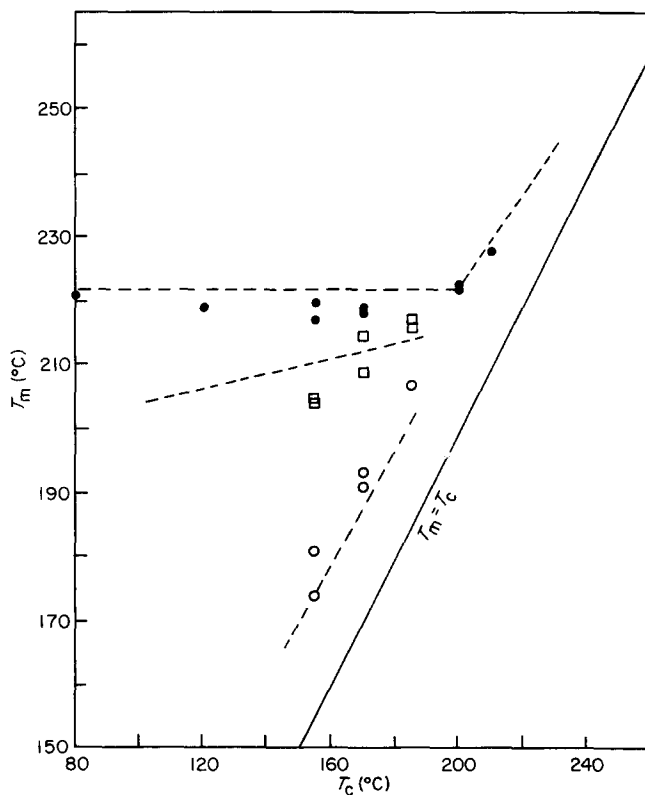


Figure 7 Melting behaviour of a blend containing 30% w/w nylon 3Me6T: (●) principal melting endotherm; (□, ○) secondary melting endotherms; (---) behaviour of nylon 6

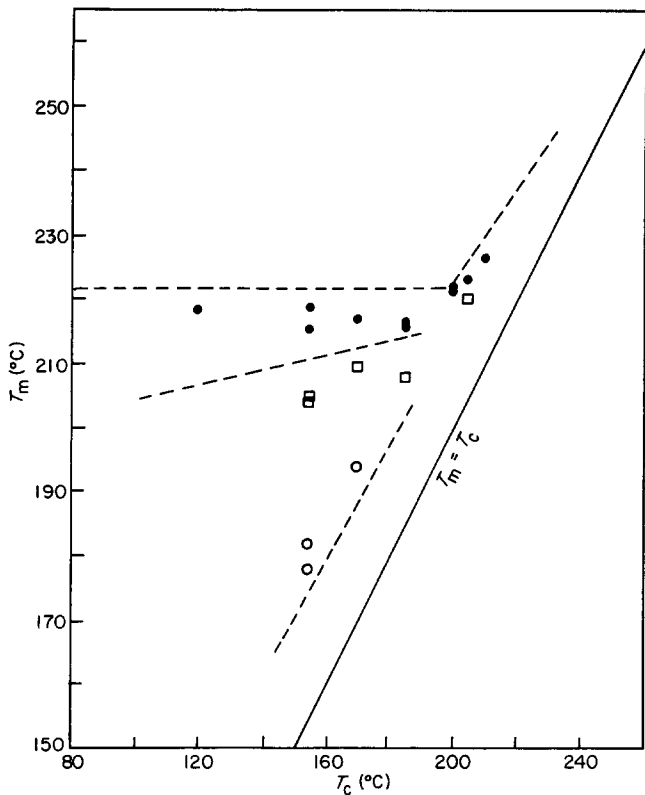


Figure 8 Melting behaviour of a blend containing 49% w/w nylon 3Me6T: (●) principal melting endotherm; (□, ○) secondary melting endotherms; (---) behaviour of nylon 6

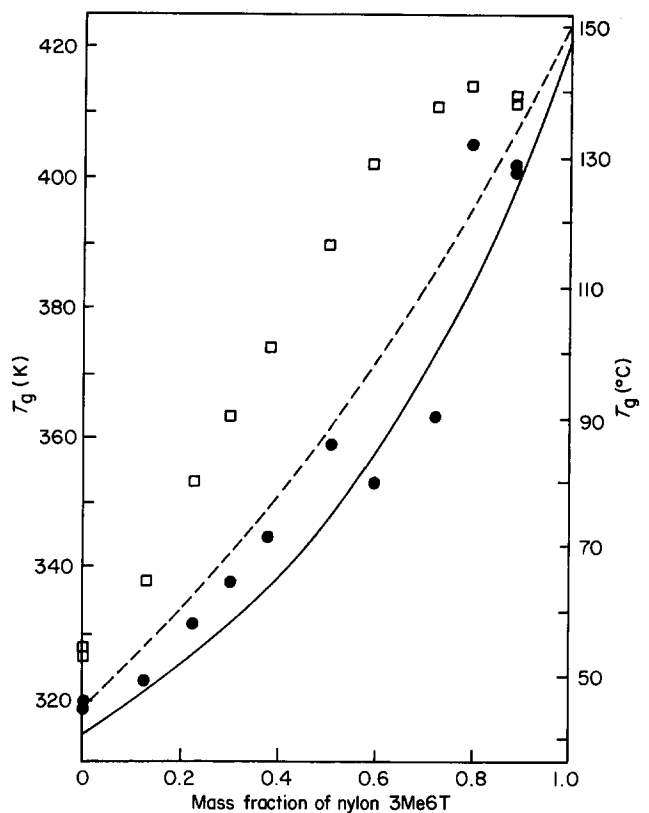


Figure 9 Comparison of the glass transition behaviour of crystallized blends, $T_c = 155^\circ\text{C}$, and that observed in the amorphous state: (●) onset T_g ; (□) midpoint T_g ; (—) amorphous onset T_g ; (---) amorphous midpoint T_g

which is reflected by an increase of T_g from that measured for the completely amorphous blends. Since the degree of crystallinity produced by annealing is independent of composition, the effect is magnified in the middle range of composition where the observed increase is greatest. An additional factor to be considered arises from the morphological influence of crystallinity on T_g . This is illustrated by the slight increase of T_g of crystallized nylon 6 over that obtained by quench cooling (see Figure 8). For the blends, however, it is not possible to separate the morphological and compositional contributions to the T_g changes observed, but it is probable that the morphological effect plays only a minor role.

The most important and unexpected feature, shown in Figures 9 and 10, is a pronounced broadening of the temperature interval associated with the glass transition. Characterized by an increasing separation of the measured onset and midpoint T_g , this interval in some cases approached in excess of 60°C . Some representative examples of this behaviour are shown in Figure 11. In some instances it was even possible to detect an apparent bimodal behaviour, as can also be seen in Figure 11. Since all of the annealing was conducted at temperatures in excess of the events observed it is possible to exclude all potentially conflicting enthalpic phenomena such as relaxation effects and melting of poorly defined crystal structures.

The completely reversible character of the transitional behaviour of the amorphous and crystallized blends suggests that the features observed are the result of a morphologically imposed heterogeneous distribution of the amorphous polymer additive within the mixed amorphous phase. The fact that this occurs to a different

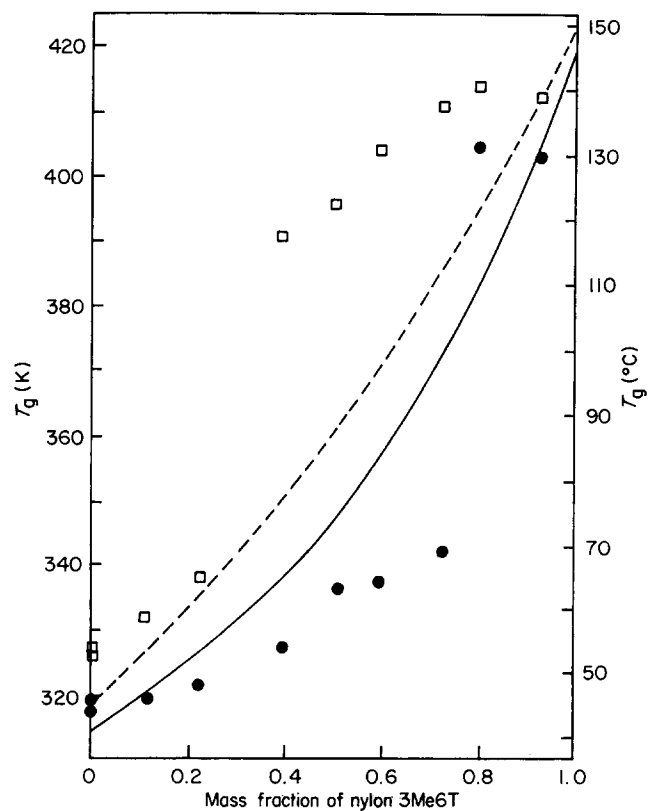


Figure 10 Comparison of the glass transition behaviour of crystallized blends, $T_c = 200^\circ\text{C}$, and that observed in the amorphous state: (●) onset T_g ; (□) midpoint T_g ; (—) amorphous onset T_g ; (---) amorphous midpoint T_g

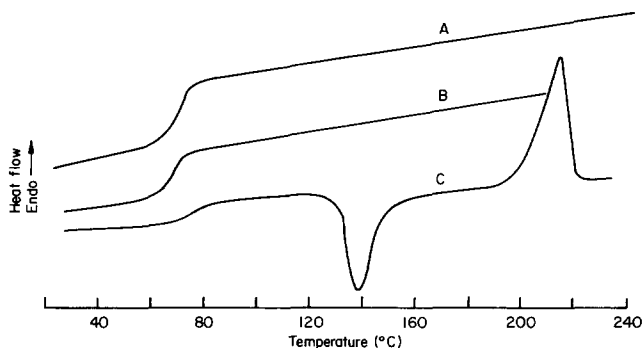


Figure 12 Representative thermograms of a blend containing 49% w/w nylon 3Me6T: A, 250°C/18 h followed by 155°C/1 h; B, 250°C/18 h quench-cooled; C, 260°C/3 min quench-cooled

blended pure components and those present in a copolymer produced by transamidation.

The nature of the interaction. A large number of fundamental short-range molecular forces have been considered to play an important role in determining the overall interaction between different polymer molecules². An obvious temptation is to speculate that an intermolecular amide–amide hydrogen-bonding interaction is the dominant element for miscibility to occur in the case of nylon 6 and nylon 3Me6T. A contradiction to this hypothesis can be provided by the results of several studies involving the blends of only semicrystalline polyamides^{7–10}. The results of these studies are not totally conclusive with regard to the mutual solution behaviour of polyamides except that immiscibility or limited miscibility is the most likely outcome on attempting to blend these polymers. Thus an amide–amide interaction may not necessarily suffice as a criterion for miscibility and perhaps a more subtle interaction is present in this particular system.

In a previous communication⁶, evidence obtained from investigating the solubility of nylon 3Me6T in the aliphatic polyamides, nylon 66, 612, 11 and 12 respectively, had allowed speculation on the correlation between chemical constitution and the resultant phase behaviour of these blends. Although not described here in detail, it has been shown that by using the criterion of a single composition-dependent T_g and by noting the influence of a miscible amorphous polymer additive on the crystallization processes of the aliphatic polyamide, nylons 66 and 612 are also both miscible with nylon 3Me6T, whereas nylons 11 and 12 are not. In all cases no *LCST* behaviour could be inferred. Thus it was suggested that the relative concentration of amide functionalities of the latter materials had a decisive influence such that a critical concentration was necessary in order for miscibility to occur. Moreover, by comparing the results obtained with those from blend studies of nylon 66 and nylon 1Me6T (ref. 38), which had also suggested miscible behaviour, it was proposed initially⁶ that the methyl substituent on the hexanediamine component may in part provide conditions for a favourable interaction.

It is now possible to refine this superficial schematic even further by including the results of blend studies involving nylon 4 and nylon 46, respectively. A more complete description and analysis of the results obtained will be presented elsewhere³⁹. However, initial studies

have indicated that nylons 4 and 46, when blended with nylon 3Me6T, each form an immiscible blend. Similarly, it has also been noted, as may be expected, that nylon 69 and nylon 610 form completely miscible blends with nylon 3Me6T. These new findings, together with those described previously, can be interpreted in terms of a recently introduced mean-field binary interaction model^{3,4}.

As mentioned previously, it is generally recognized that in order for two polymers to be miscible, an exothermic interaction, i.e. a negative value of the Flory interaction parameter χ_{12} , is a primary requirement. Other prerequisites are also necessary. However, it has been suggested that in some instances miscibility may be rationalized by treating polymers as copolymers composed of appropriate chemical functionalities which define the polymers in question as random copolymers. This type of approach has produced a great deal of success in accounting for a large body of observations concerning miscibility of polymer blends^{40–43}. Using the same formalism and notation of ten Brinke *et al.*⁴ it is possible to obtain the familiar Flory–Huggins expression for the Gibbs free energy of mixing of two copolymers A_xB_{1-x} and C_yD_{1-y} in the form:

$$\begin{aligned} \Delta G/RT = & (\phi_1/N_1) \ln \phi_1 + (\phi_2/N_2) \ln \phi_2 + \phi_1\phi_2 [xy\chi_{AC} \\ & + (1-x)y\chi_{BC} + x(1-y)\chi_{AD} + (1-x)(1-y)\chi_{BD} \\ & - (1-x)\chi_{AB} - y(1-y)\chi_{CD}] \end{aligned} \quad (2)$$

In equation (2) x and y represent copolymer compositions expressed as volume fractions of the respective mers of the copolymers of blend volume fractions ϕ_1 and ϕ_2 , respectively. The degrees of polymerization N_1 and N_2 are a measure of molecular weight of polymers 1 and 2, respectively. The various χ_{ij} , as denoted by their subscripts, represent segmental interaction parameters. Using this type of notation, where the phase behaviour is governed by the sign of the function, $f(\chi_{ij})$, it is possible to write an expression for the interaction parameter, χ_{blend} , for a mixture of copolymers A_xB_{1-x} and $A_yB_zC_{1-y-z}$ as:

$$\begin{aligned} \chi_{blend} = & [(1-x)(y-z) + z(x-y)]\chi_{AB} + (1-y-z)(1-x-z)\chi_{BC} \\ & + (1-y-z)(x-y)\chi_{AC} \end{aligned} \quad (3)$$

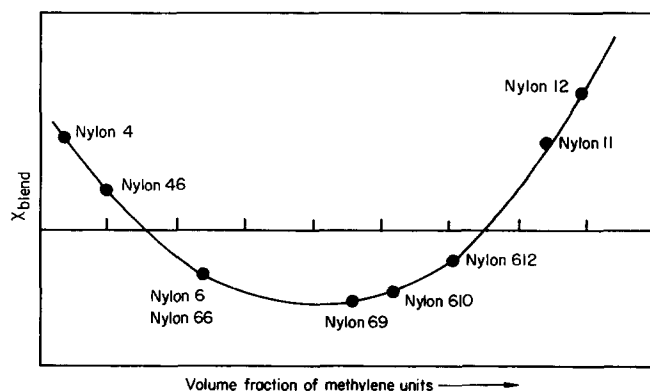


Figure 13 Schematic representation of χ_{blend} as a function of composition of the aliphatic polyamide (A_xB_{1-x}) for blends containing nylon 3Me6T

In this case there are only three segmental interaction parameters and for fixed values of y and z the equation above is a quadratic function of x . The foregoing becomes significant if it is assumed that aliphatic polyamides can be rationalized as copolymers of methylene (A) and amide (B) functionalities and the nylon 3Me6T is a terpolymer of methylene, amide and phenyl (C) functionalities. Such a simplification requires the methyl groups of the nylon 3Me6T to interact in an equivalent manner to methylene groups. Thus with suitable values of χ_{ij} , the mathematical nature of equation (3) can be reconciled with the experimentally observed phase behaviour as shown schematically in *Figure 13*. Similar observations to these have been treated in an identical manner to that described here, but in the former case the homologous series of polymers was provided by a series of polyesters blended with poly(vinyl chloride)⁴³. Further experiments and calculations are in progress in order to quantify this sketch of polyamide blend phase behaviour, which will form the subject of a future publication³⁹.

CONCLUSIONS

A detailed thermoanalytical study, in unison with morphological observations, has shown that nylon 6 forms a miscible blend with the aromatic polyamide, nylon 3Me6T, across the entire range of composition. Preliminary investigations have also indicated that blends containing nylon 66, nylon 69, nylon 610 and nylon 612 will also behave in a similar manner. The observed immiscibility of nylon 3Me6T in the nylons 4, 46, 11 and 12, respectively, defines a window of miscibility with an upper-bound and a lower-bound concentration of amide functionalities. This new and unexplored area of miscible blends is of potential practical interest. However, these findings are particularly significant when viewed within the context of the type of interactions that can exist between different polymer molecules. Some interpretations of polymer-polymer miscibility have been advanced using a framework derived from favourable associative interactions of a hydrogen-bonding nature. The miscible blends cited here can certainly be considered to fall within this category. However, it has been shown for example that the composition dependence of the glass transition temperature is in excellent accord with a theoretical prediction which does not rely on the inclusion of such phenomena. Further studies of the polyamide blends described here may help to resolve some of these important questions.

It has also been shown that the innate ability of the nylon 6 component to crystallize is not suppressed within the blends even in the dilute regime. The expected influence of this phenomenon on the mixed amorphous phase was complicated by an unusual broadening of the glass transition, particularly in the middle of the composition range. Although it has been suggested that this phenomenon is attributable solely to a morphological effect, further studies should be initiated to investigate this behaviour, and to establish if it forms a common feature of miscible amorphous/semicrystalline blends in general. Finally, it has been proposed that the influence of aliphatic polyamide composition on the solution behaviour of the aromatic polyamide can be

correlated and formulated within the terms of a binary interaction model. A quantitative account of the application of this model is currently under development and will form the subject of a future communication.

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