Blends of aliphatic polyamides with a trifluoromethyl-substituted polyaramide

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The effect of trifluromethyl group substitution on the thermal properties of blends of a polyaramide with several aliphatic polyamides has been determined. Miscibility of the substituted polyaramide with nylons 46, 6, 66, 69, 610 and 11 was shown by the existence of single, composition-dependent glass transition temperatures (T_gs) and composition-dependent crystalline melting temperatures (T_ms). The results are discussed with reference to T_g and T_m predictive equations.

(Keywords: polyaramide; nylon; blend; molecular composite; trifluoromethyl; miscibility)

INTRODUCTION

The blending of two disparate polymers to achieve a new material with the desirable properties of both polymers has been the subject of much research in recent years. In particular, the blending of a rod-like polymer with an amorphous or semicrystalline polymer to yield a molecular composite is of interest. These blends could be expected to have properties similar to fibre-reinforced composites without the disadvantages inherent with the presence of fibre–polymer interfaces. The blending of rigid rod polyaramides, e.g. poly(phenylene terephthalamide), with aliphatic polyamides (nylons) has received considerable attention[1–14]. The effects of the incorporation of the hexafluoro-isopropylidene group into polyimides used in polyimide blends have also been reported[15,16]. We were interested in enhancing the miscibility of polyaramides with nylons; and recent research reported by Gaudiana *et al.*[17–19] on the solution properties of trifluoromethyl-substituted polyaramides encouraged us to investigate the effects of this structure modification on polymer/polymer miscibility.

In this paper, the effects of trifluoromethyl group substitution on the miscibility of a polyaramide with several nylons is reported.

EXPERIMENTAL

General

N-Methylpyrrolidinone (b.p. 202–204°C) and 1,1,3,3-tetramethylurea (b.p. 174–176°C) were fractionally distilled under argon from calcium hydride and stored under argon in bottles with septum inlets. Anhydrous *N*,*N*-dimethylacetamide (Aldrich) was used as received. Lithium chloride was dried at 0.05 torr and 135°C for 2 h immediately before use. 2,2′-Bis(trifluoromethyl)benzidine (m.p. 181–182°C, lit. m.p. 181–182°C (ref. 18)), terephthaloyl chloride (m.p. 80–81°C) and benzidine (m.p. 127–129°C) were dried and stored in a glove box. All apparatus was dried at 170°C overnight and cooled in an argon atmosphere.

Nylon 46 (Allied), nylon 6 (Polysciences), nylon 66 (Du Pont), nylon 69 (Aldrich), nylon 610 (Aldrich), and nylon 11 (Atochem) were dried at 0.05 torr before use. These polymers had number average molecular weights in the range of 12 000 to 30 000.

Polymer synthesis

In general, the method of Rogers *et al.*[18] for obtaining high molecular weight polymer was used. However, by controlling the stoichiometry, time and temperature of the polymerization, a lower molecular weight was obtained. For example, a poly[2,2′-bis(trifluoromethyl)-4,4′-biphenylenephenylene dicarboxamide] (TFMBPP) of approximately 40 000 molecular weight could be obtained as follows. A 2 l Morton flask equipped with a mechanical stirrer, argon inlet/outlet, addition funnel and thermometer was used to contain *N*-methylpyrrolidinone (210 ml) and 1,1,3,3-tetramethylurea (210 ml) under an argon atmosphere. Lithium chloride (30.5 g) was quickly added to the rapidly stirred solvent pair. After dissolution was accomplished, the clear solution was cooled to −5°C. During cooling, 2,2′-bis(trifluoromethyl)benzidine (17.61 g, 55.0 mmol) was quickly added. When −5°C was reached, terephthaloyl chloride (10.15 g, 50.0 mmol) was quickly added, followed by cold 1,1,3,3-tetramethylurea (210 ml). The temperature rose to 0°C before returning to −5°C. The very viscous brown solution was stirred at −5°C for 30 min and 0°C for 30 min before precipitating the polymer into hot water. The polymer was washed first with hot water and then with acetone before drying at 135°C and 0.05 torr. Analysis for lithium showed that all lithium chloride had been removed. An inherent viscosity of 2.025 was obtained and low angle light scattering measurements indicated a molecular weight of about 40 000. A density of 1.47 g cm^{-3} was determined. In a similar manner, poly[4,4′-biphenylenephenylene dicarboxamide] (BPP) was synthesized from benzidine and terephthaloyl chloride.

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Polymer characterization

Inherent viscosities were determined at 30°C in *N*,*N*-dimethylacetamide containing 5 wt% lithium chloride. Low angle light scattering was done in *N*,*N*-dimethylacetamide with a Dawn model F laser LS photometer by Scientific Polymer Products, Inc. Density was determined with a CMI Micrometrics autopycnometer, model 1320. The autopycnometer was standardized and analysis of a nylon 610 sample gave a density of 1.05 (lit. 1.05[20]).

Thermal analysis

Thermal analysis was conducted at a heating rate of $10°\mathrm{C\,min^{-1}}$ using a Perkin-Elmer Series 7 differential scanning calorimeter (d.s.c.) calibrated for temperature and enthalpy using indium. The sample was first heated to a temperature above the T_m for 2 min (nylon, *T*: 46, 300°C; 6, 250°C; 66, 300°C; 69, 250°C; 610, 250°C; 11, 250°C). This was followed by a liquid nitrogen quench. Data were collected on the next heating run.

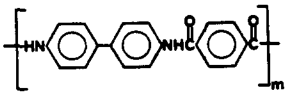
Equilibrium melting temperatures (T_m° and T_{mb}°) were obtained by heating the sample at $10°\mathrm{C\,min^{-1}}$ to a temperature above the T_m (250°C for nylon 6 and 300°C for nylon 46). After 2 min at this temperature the sample was quenched at $200°\mathrm{C\,min^{-1}}$ to the annealing temperature (170°C for nylon 6 and 230°C for nylon 46). Each sample was annealed for 16 h before quenching to 0°C and running a heating scan at $10°\mathrm{C\,min^{-1}}$.

Polymer blend preparation

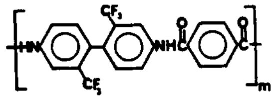
Volumetric 1 wt% solutions in sulfuric acid were combined titrimetrically and stirred for 24 h. The transparent, single phase blend solutions were precipitated in hot water and the coagulated polymers were washed to a neutral pH. After washing three times with diethyl ether, the blends were dried at 0.05 torr for at least 24 h at 110°C.

RESULTS AND DISCUSSION

Two polymers were prepared for this study. Poly(4,4′-biphenylenephenylene dicarboxamide) (BPP) is an analogue of the rigid rod polymer Kevlar and in a similar manner is insoluble in most solvents. The other polymer, poly[2,2′-bis(trifluoromethyl)-4,4′-biphenylenephenylene dicarboxamide] (TFMBPP) has trifluoromethyl substitution on the aromatic groups of the polymer backbone. The effect of these groups is twofold: (1) the overall polar nature of the polymer is changed to have a potentially more desirable interaction with other polymers and (2) the bulkiness of the trifluoromethyl groups modifies the linearity of the polymer chain. In addition to affecting the solubility characteristics in organic solvents, the insertion of trifluoromethyl groups lowers the T_gs. The unsubstituted polymer (BPP) has a T_g of 265°C while the T_g for TFMBPP is 228°C (*Figure 1*). The glass transitions for both polymers are very broad. The respective heat capacities (ΔC_ps) are 0.10 and $0.17\ \mathrm{J\,g^{-1}\,°C^{-1}}$. Although not shown in *Figure 1*, both polymers were subjected to temperatures up to decomposition. There was no evidence for a crystalline melting point.



BPP



TFMBPP

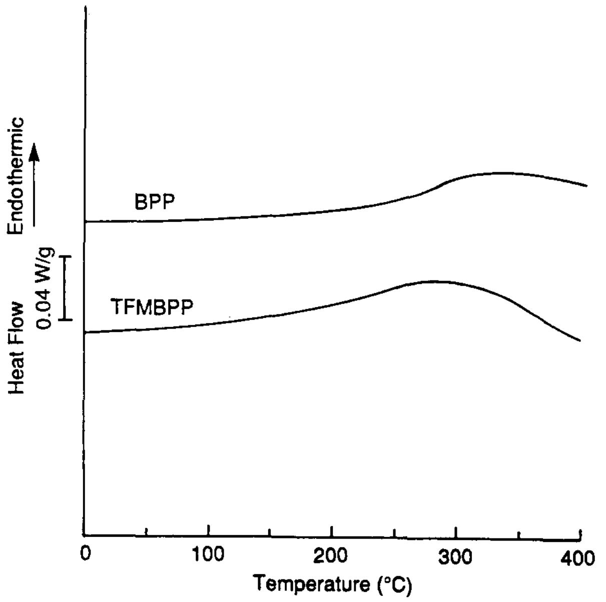


Figure 1 Thermal traces of aromatic polyamides (2 min at 400°C, followed by quench cooling in liquid nitrogen)

The method chosen for determining polymer/polymer miscibility is that of the effect of composition on T_g. One major concern that exists when polyamide blends are subjected to temperatures above the melting point is that transamidation will occur. It has been shown recently[21] that transmidation can take place and will cause homogenation of an otherwise immiscible blend under certain temperature conditions. Takeda and Paul prepared blends of an aliphatic–aromatic polyamide, poly(*m*-xylene adipamide), and nylon 6 by extrusion at 260 and 290°C. Extrusion at a temperature about 40°C above the melting point of nylon 6 yielded two glass transition temperatures, while extrusion at temperatures about 70°C above the melting point developed a blend with one glass transition temperature. Time and temperature studies showed that a period of 42 min was required at 260°C to create homogeneity. In the experimental procedure used in this research, all thermal pretreatments were limited to minimal times at temperatures above T_m of the aliphatic polyamide and T_g of the polyaramide. The blends containing nylons 6, 69, 610 and 11 were subjected to the least severe thermal conditions, i.e. 2 min at 250°C. The blends containing nylon 46 and nylon 66 were heated to 300°C for 2 min to ensure complete melting of these high melting polyamides, 290°C and 269°C, respectively. A progressive time and temperature study with temperatures up to 300°C was carried out with the nylon 6 blends and virtually no changes in the single glass transition temperature were noted. Also, the TFMBPP is a wholly aromatic polyamide which would be more resistant to transamidation reactions than an aliphatic–aromatic polyamide, such as poly(*m*-xylene adipamide). With this approach of minimal thermal treatment, the possible effect of transamidation reactions on the observed miscibility of these aliphatic–aromatic polyamide blends would tend to be negated.

Several aliphatic polyamides were chosen as matrices for the rigid rod polymers. These polyamides differ in the number of methylene groups in the backbone and, thus, vary from the unethylene-like nylon 46 to the more ethylene-like nylon 11. The aliphatic polyamides also differ greatly in their ability to crystallize, e.g. nylon 46 crystallizes so rapidly from the melt that it is not possible to suppress the amount of crystallinity. The other polymers have slower rates of crystallization, and thus various degrees of crystallinity when quenched from the melt. These properties can affect the relative miscibilities of the nylon/rigid rod polymer pairs.

Blends of BPP with aliphatic polyamides

Since BPP contains a biphenyl group and, therefore, has slightly more flexibility than a purely rigid rod like Kevlar, it might show some miscibility. The effect of blending BPP with the very amide-like nylon 46 on various thermal properties is shown in *Table 1*. Even at a 50/50 composition there is virtually no change in thermal properties. Similar results were obtained with nylon 6. The T_g is essentially unaffected by blend composition. As will be seen later for miscible blends, both the crystallization temperature (T_c) of the crystallizable portions of nylon 6 and the melting temperature (T_m) can be strongly affected by blend composition. BPP, however, is not miscible with nylon 6 and does not affect the T_g, although a small depression of T_m is observed.

Blends of TFMBPP with aliphatic polyamides

The thermal traces from 0 to 300°C are shown in *Figure 2* for a series of blends of nylon 46 and TFMBPP covering the compositional range of 100/0, 90/10, 80/20, 70/30, 60/40, 50/50 and 40/60, where 100/0 is pure nylon 46. Although it is difficult to see changes in T_g on this scale the effects on the crystalline portion of the nylon 46 are marked. Two crystalline melting peaks are shown at 279 and 290°C. As the concentration of TFMBPP is increased the areas of the melting peaks decrease, coalescing into one peak for the 80/20 blend and continually broadening. Also the melting temperature becomes increasingly depressed with increasing concentrations of TFMBPP. It is interesting to note the lack of a crystallization endotherm. Nylon 46 crystallizes so rapidly from the melt that not even liquid nitrogen quenching can prevent excessive crystallization. Even on this scale T_g can be seen to increase with increasing rigid rod concentration. Effects on T_g are more readily seen in *Figure 3*. With this expanded scale small changes in the nylon 46 T_g are observed up to about a 60% content of TFMBPP. For the 30/70 and higher blends the T_g changes more dramatically. In *Table 2* are listed the thermal properties of the 100/0 and 50/50 blends including onset and midpoint T_g temperatures.

A complete composition range of blends of nylon 6 and TFMBPP was also prepared. The thermal traces for the 100/0, 90/10, 80/20 and 70/30 blends are presented in *Figure 4*. For these blends the observed T_g increases and broadens with increasing TFMBPP content. The crystallization temperature and melting temperature increase and decrease, respectively, while the peaks broaden for both transitions. When 40 wt% TFMBPP is incorporated into the blend, a T_c can no longer be determined although a small T_m is still observed. Crystallization is completely suppressed in the blends with higher TFMBPP contents. The effect of composition on T_g is shown more clearly in *Figure 5*. The T_g is found to continually increase with increased rigid rod content

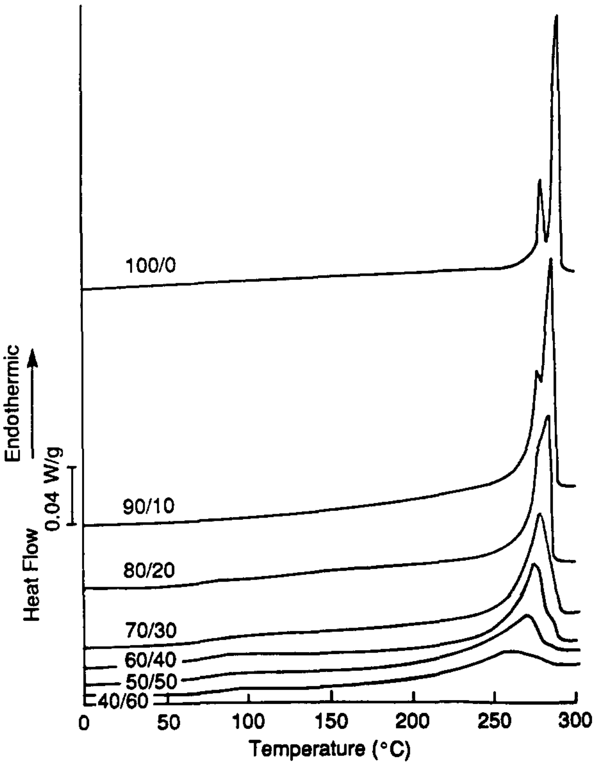


Figure 2 Thermal traces of 100/0 to 40/60 nylon 46/TFMBPP blends

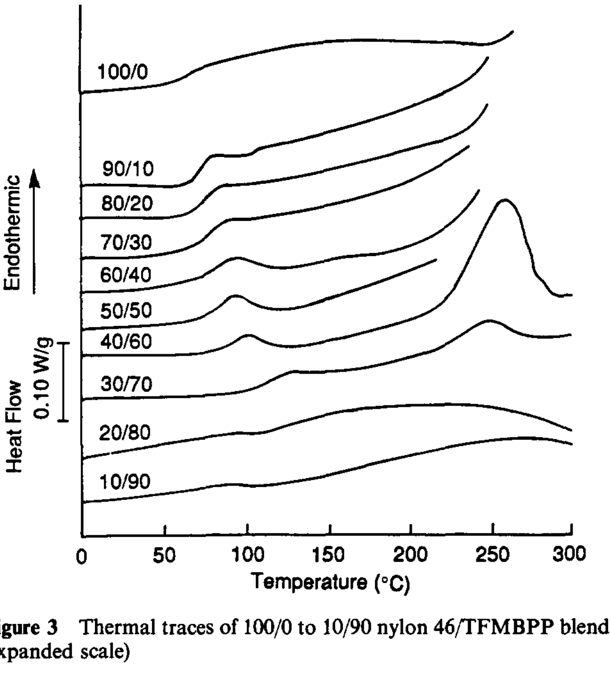


Figure 3 Thermal traces of 100/0 to 10/90 nylon 46/TFMBPP blends (expanded scale)

Table 1 Thermal properties of nylon 46 and nylon 6 blends with BPP

		T_g (°C)		T_c (°C)		T_m (°C)	
Nylon	Blend	Onset	Midpoint	Onset	Peak	Onset	Peak
46	100/0[a]	55	63	–	–	ND	290[c]
46	50/50[a]	56	69	–	–	ND	286
6	100/0[b]	42	46	61	69	190	223
6	50/50[b]	31	47	–	–	ND	219

[a] Samples were heated at 300°C for 2 min before quenching in liquid nitrogen. Scans were run at 10°C min^{-1}

[b] Samples were heated at 250°C for 2 min before quenching in liquid nitrogen. Scans were run at 10°C min^{-1}

[c] Minor melting peak at 279°C

ND, not determined

Table 2 Thermal properties of nylon blends with TFMBPP

		T_g (°C)		T_c (°C)		T_m (°C)	
Nylon	Blend	Onset	Midpoint	Onset	Peak	Onset	Peak
46[a]	100/0	55	63	–	–	ND	290[e]
46[a]	50/50	67	78	–	–	ND	269
6[b]	100/0	42	46	61	69	190	223
6[b]	60/40	62	77	–	–	ND	202
		61[b]	78	–	–	ND	205
		64[c]	80	–	–	ND	204
		66[a]	78	–	–	ND	200
		61[d]	81	–	–	ND	202
6[b]	50/50	67	87	–	–	–	–
66[a]	100/0	44	48	83	91	233	269
66[a]	50/50	68	77	–	–	ND	236
69[b]	100/0	32	36	50	58	193	213
69[b]	50/50	76	88	–	–	–	–
610[b]	100/0	33	36	46	56	191	221
610[b]	50/50	73	80	–	–	ND	200
11[b]	100/0	15	25	36	47	139	190
11[b]	50/50	75	87	–	–	ND	168

[a] Samples were heated at 300°C for 2 min
[b] Samples were heated at 250°C for 2 min
[c] Sample was heated at 280°C for 2 min
[d] Sample was heated at 300°C for 1 min
[e] Minor melting peak at 279°C
ND, not determined
All samples were quenched in liquid nitrogen and scans were run at 10°C min^{-1}

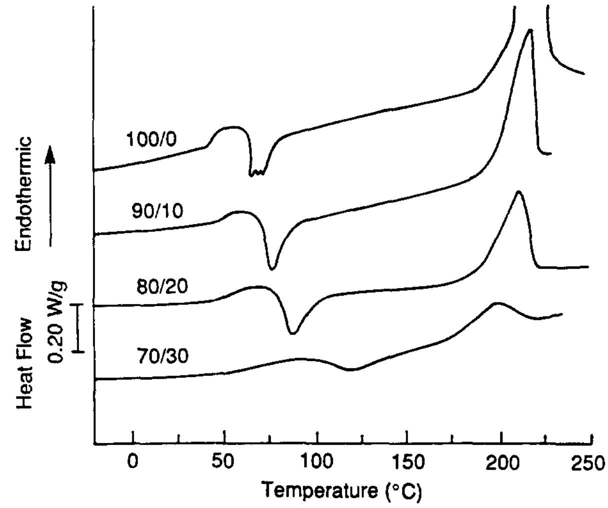


Figure 4 Thermal traces of 100/0, 90/10, 80/20 and 70/30 nylon 6/TFMBPP blends

and to change from a sharp transition to a very broad one. Generally, local fluctuations in the blend composition of the amorphous phase cause broadening of the glass transition. The thermal properties of the 100/0 and 50/50 blends are included in *Table 2*. Also included are the results of a temperature study to determine whether or not the pre-quench heating over the range of 230 to 300°C would have any effect on thermal properties. For the 60/40 blend there is virtually no effect of heating conditions on the resulting T_g or T_m. Similar results were obtained for these heating conditions when used for the 50/50 blend.

The thermal properties of the 100/0 and 50/50 nylon 66/TFMBPP blends are shown in *Table 2*. The T_g of the nylon 66 is strongly affected by blending with TFMBPP. The T_g is increased by 29°C, the crystallization temperature could not be determined and the melting temperature was lowered by 33°C.

The complete range of blend compositions from 100/0 to 0/100 were analysed for the nylon 69/TFMBPP combination. *Figure 6* shows the thermal traces for these blends over the temperature range of −20 to 250°C. On this scale the T_g and its movement to higher temperatures with increasing TFMBPP content is easily observable only for nylon 69 rich blends so only the 100/0, 90/10, 80/20 and 70/30 blends are shown. Also, the crystallization peak is found to move to higher temperatures. The effect of blend composition on the crystallization of nylon 69 is much larger than with the other blends. As the TFMBPP content increases the T_m is decreased in temperature and area with some broadening. As with the other blends, the addition of TFMBPP rapidly suppresses the crystallization of the nylon, the exception being nylon 46 which still exhibits

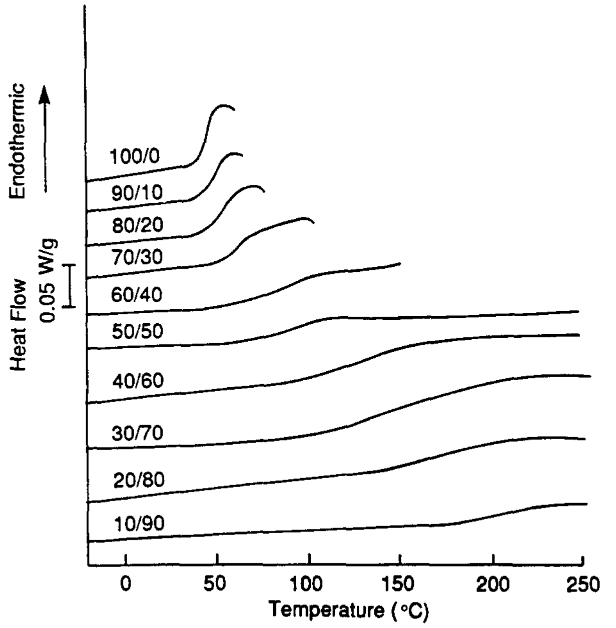


Figure 5 Thermal traces of 100/0 to 10/90 nylon 6/TFMBPP blends (expanded scale)

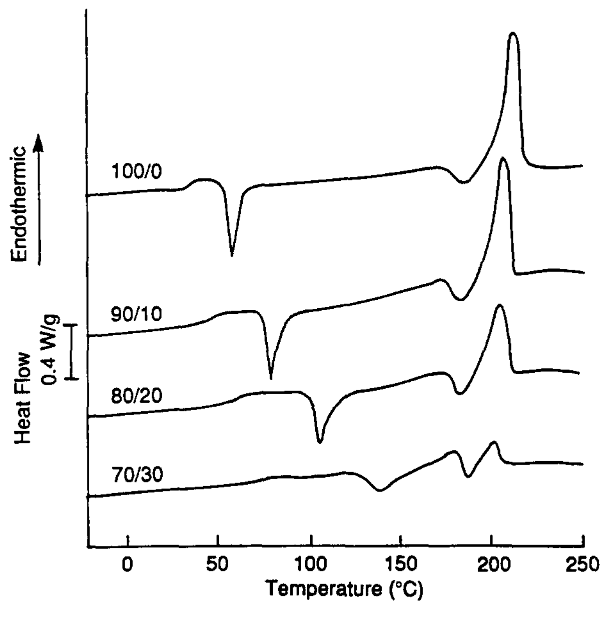


Figure 6 Thermal traces of 100/0, 90/10, 80/20 and 70/30 nylon 69/TFMBPP blends

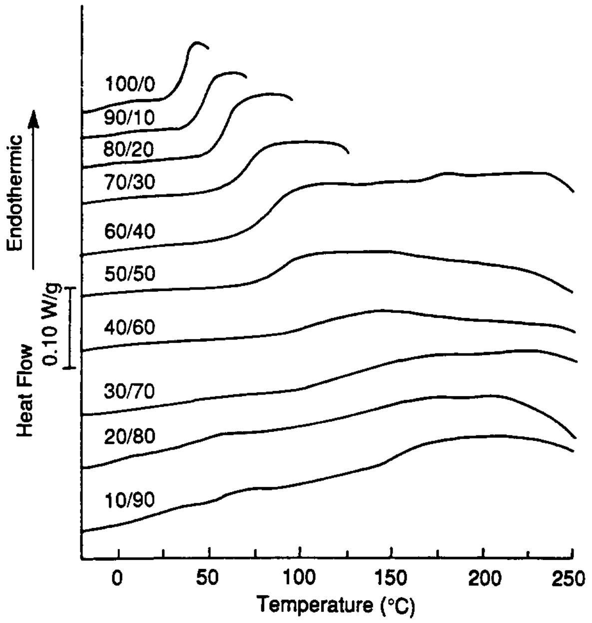


Figure 7 Thermal traces of 100/0 to 10/90 nylon 69/TFMBPP blends (expanded scale)

a T_m with the 30/70 blend. With higher TFMBPP contents the thermal traces are essentially featureless on the scale used in *Figure 6*. Changes in T_g are better shown in *Figure 7* where the constant increase in temperature with TFMBPP concentration is observed. Unlike nylon 46 which showed only small changes in T_g at low TFMBPP concentrations, the T_g of nylon 69 is markedly affected with incremental changes of 11°C, 14°C, etc., with each 10% increase in rigid rod concentration. The thermal properties of the 100/0 and 50/50 blends are shown in *Table 2*.

The thermal properties of a 50/50 blend of nylon 610 with TFMBPP are compared with the pure nylon 610 in *Table 2*. The incorporation of 50 wt% rigid rod increases the T_g by as much as 44°C and lowers the melting temperature by about 21°C.

The effects of TFMBPP concentration on the thermal responses of nylon 11 were determined. The thermal traces of a complete composition range of nylon 11/TFMBPP blends over the temperature range of -20 to 250°C are shown in *Figure 8*. The glass transition temperature is seen to move to increasingly higher temperatures with increasing TFMBPP content. For the 100/0 to 70/30 blends the T_c also increases whereas the T_m peak moves to lower temperatures, decreases in size and broadens. Again, as with the other blends, the addition of TFMBPP first suppresses, then eliminates the ability of the nylon to crystallize. The larger scale of *Figure 9* shows the changes in T_g more clearly. The thermal properties of the 100/0 and 50/50 blends are listed in *Table 2*. As observed for the other aliphatic polyamide blends, the T_g increases with incremental changes in TFMBPP content. The crystallization temperature increases by 58°C with a 40 wt% increase in TFMBPP and disappears completely in the 50/50 blend. The T_m decreases by about 22°C over the range of 100/0 to 50/50.

The existence of one, composition-dependent glass transition temperature for a blend of two pure polymers is sufficient proof of polymer compatibility. With a miscible pair of polymers the local molecular environment between polymer chains is the same as that of adjacent monomer units on the same chain. Using this criterion, the blends of nylon 46, 6, 66, 69, 610 and 11 with TFMBPP are considered to be miscible. The fact that blends of BPP are not miscible proves the efficiency of trifluoromethyl substitution for improving blend miscibility.

Prediction of blend T_g

The T_g–composition dependency can be predicted, to some extent, by application of the Couchman equation[22,23]. This theoretical equation is based on the assumption that there is random mixing of the two polymers at the segmental level. This relationship, shown below, has been successfully used to predict

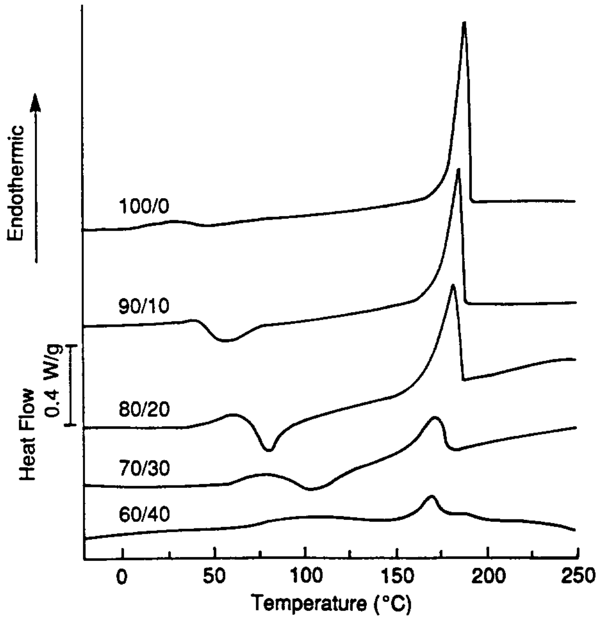


Figure 8 Thermal traces of 100/90, 90/10, 80/20, 70/30 and 60/40 nylon 11/TFMBPP blends

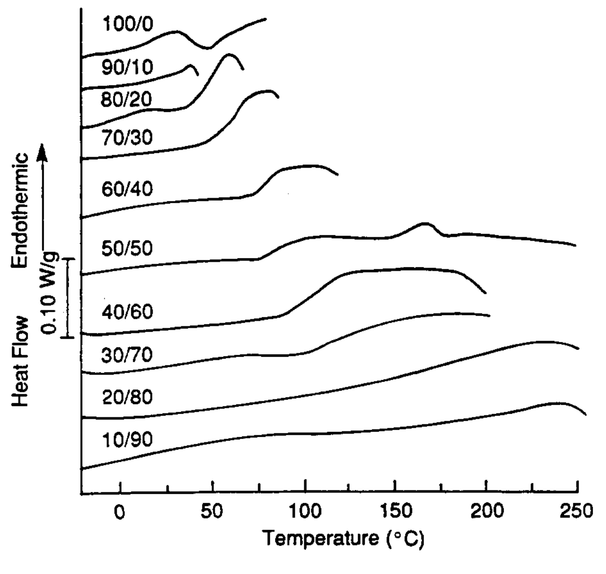


Figure 9 Thermal traces of 100/0 to 10/90 nylon 11/TFMBPP blends (expanded scale)

T_g–composition behaviour for a number of polymer pairs.

$$\ln T_{gb} = \frac{x_1 \Delta C_{p1} \ln T_{g1} + x_2 \Delta C_{p2} \ln T_{g2}}{x_1 \Delta C_{p1} + x_2 \Delta C_{p2}} \tag{1}$$

In this equation, T_{gb}, T_{g1} and T_{g2} are the glass transition temperatures of the blend, homopolymer 1 and homopolymer 2, respectively. Similarly, x_1 and x_2 are the mass fractions and ΔC_{p1} and ΔC_{p2} are the incremental changes in heat capacity at T_g of the pure homopolymers. A precise experimental determination of ΔC_p for completely amorphous aliphatic nylons is not possible due to the masking effect of the competing crystallization process at a temperature very close to T_g. This is especially true in the case of nylon 6. An additional factor that makes the experimental determination of ΔC_p imprecise is the tendency of the aliphatic nylon to crystallize to some extent even when quenched in liquid nitrogen directly from the melt. Approximate values of these incremental heat capacities can be calculated by the method of Gaur and Wunderlich[24]. This method was established by the analysis of literature data of a very large number of diverse materials. Using the concept that the change in heat capacity can be related to the smallest molecular unit (bead) where movement can cause an effect, approximate incremental heat capacities can be calculated: nylon 46, 0.590; nylon 69, 0.654; and nylon 11, 0.702. The units are $\mathrm{J\,g^{-1}\,K^{-1}}$. In this system the value per bead is $\simeq 11.7\,\mathrm{J\,mol^{-1}\,K^{-1}}$. Nylon 6, for example, would have 6 'beads' and a ΔC_p of $0.623\,\mathrm{J\,g^{-1}\,K^{-1}}$.

Figures 10–13 show plots of T_g calculated by equation (1) as well as the experimentally determined T_g. Midpoint T_gs are used. The agreement between the predicted T_g and measured T_g is very close for the nylon 46/TFMBPP blend (*Figure 10*). The nylon 6 (*Figure 11*) and nylon 69 (*Figure 12*) blends show slightly larger deviations. The nylon 11 blend (*Figure 13*) qualitatively shows the largest deviation. There differences could be due to factors not considered in equation (1), i.e. changes in polarity of the aliphatic nylons, differences in the availability of hydrogen bonding between the different nylons and TFMBPP, imprecise determination of ΔC_p of the very broad T_g of the TFMBPP, etc. Nylon 11 has a much larger ethylenic character than nylon 46 and, qualitatively, may be less miscible with TFMBPP. In a similar manner, if hydrogen bonding does play a role in the miscibility of these polymers, then nylon 46 has a larger number of hydrogen bonding sites per chain length than does nylon 11, and could be more miscible with TFMBPP.

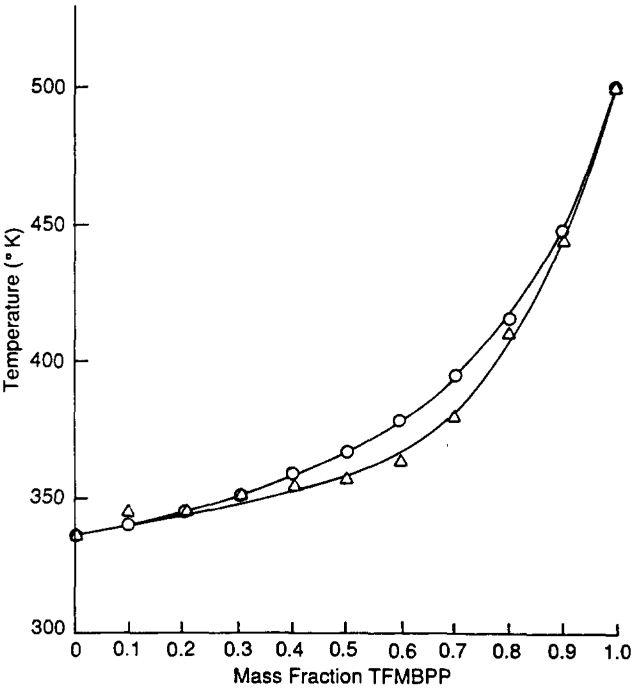


Figure 10 Glass transition behaviour of nylon 46/TFMBPP blends: (△) midpoint T_g; (○) midpoint T_g (calculated by equation (1))

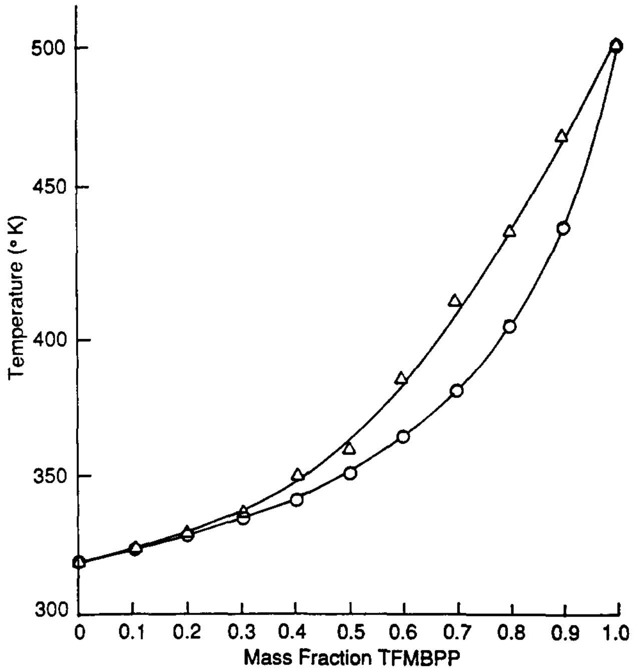


Figure 11 Glass transition behaviour of nylon 6/TFMBPP blends: (△) midpoint T_g; (○) midpoint T_g (calculated by equation (1))

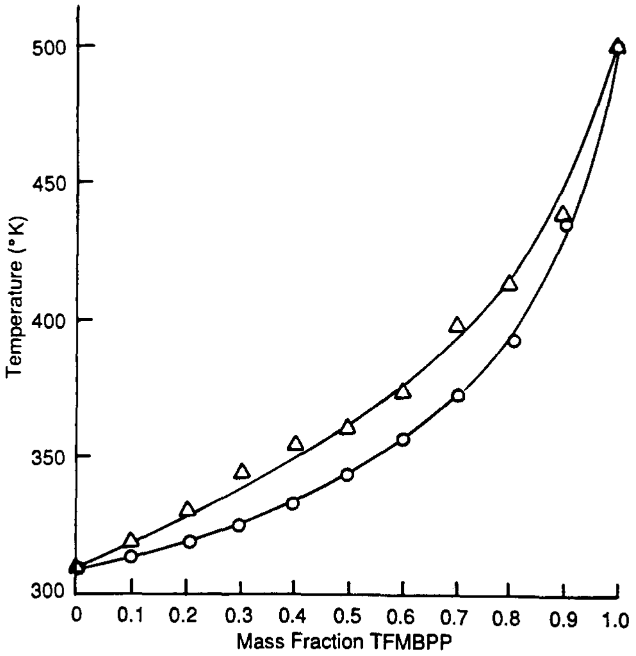


Figure 12 Glass transition behaviour of nylon 69/TFMBPP blends: (△) midpoint T_g; (○) midpoint T_g (calculated by equation (1))

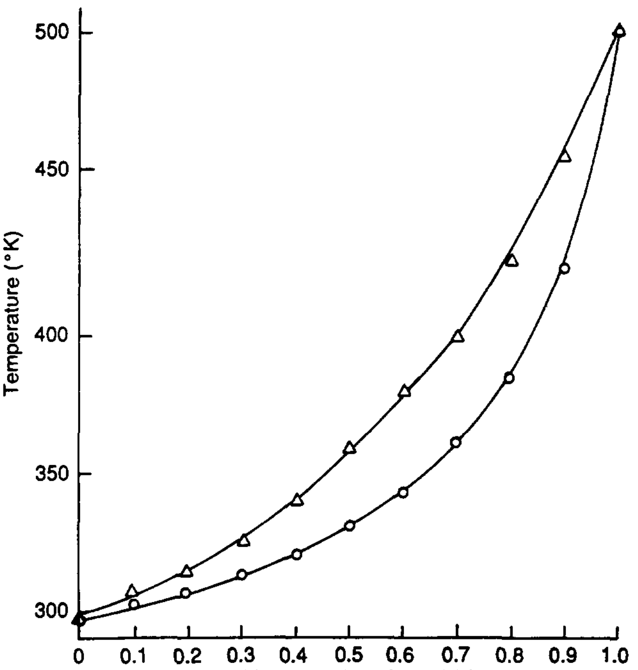


Figure 13 Glass transition behaviour of nylon 11/TFMBPP blends: (△) midpoint T_g; (○) midpoint T_g (calculated by equation (1))

Prediction of melting temperature depression

Another characteristic feature of miscible crystalline amorphous blends is a depression of the melting temperature (T_m) as a result of the diluent effect of the amorphous polymer. This effect can be quite large as, for example, with the nylon 46/TFMBPP blend where the T_m drops 43°C before a non-crystallizable blend is obtained. The inability of blends with a high amorphous polymer content to crystallize explains, in part, the large drop in T_m. A severe kinetic restriction on the crystallization process results since the T_g of the low T_g, crystallizable polymer increases as more and more of the high T_g amorphous polymer is incorporated. The continued separation of crystallizable chains by amorphous chains with increased amorphous content has an end result that the critical nucleus size needed for crystallization is no longer available. This point of non-crystallization varies with the structure of each aliphatic polymer.

Assuming that the T_m depression is due to a diluent effect and not from changes in crystalline morphology, then using the Flory–Huggins equation[25], it is possible to predict the melting point dependence on blend composition. Following the treatment of Nishi and Wang[26], if both polymers are high molecular weight (m_1, $m_2 \gg 1$), then the melting point depression in a miscible blend can be written as

$$\left(\frac{1}{T^\circ_{mb}}-\frac{1}{T^\circ_{m}}\right)=\frac{-Rv_2}{v_1\Delta H_2}[\chi(1-\phi_2)^2] \qquad (2)$$

where T°_{mb} and T°_m are the equilibrium melting points of the blend and homopolymer, respectively; ΔH_2 is the heat of fusion for the 100% crystalline homopolymer; v_1 and v_2 are the molar volumes, ϕ_1 and ϕ_2 are the volume fractions. χ is the blend interaction parameter. If entropic contributions to χ are ignored, then

$$\chi=\frac{Bv_1}{RT} \qquad (3)$$

where B is the interaction density. Combination of equations and rearrangement with $T=T^\circ_{mb}$ yields the following

$$\left(1-\frac{T^\circ_{mb}}{T^\circ_{b}}\right)=\frac{-Bv_2}{\Delta H_2}(1-\phi_2)^2 \qquad (4)$$

Thus, a plot of $(1-T^\circ_{mb}/T^\circ_m)$ *versus* $(1-\phi_2)^2$ should give a straight line with a slope of $-Bv_2/\Delta H_2$. Calculating for the interaction density and substituting in equation (3) yields χ. The equilibrium melting points, T°_m and T°_{mb}, can be obtained in many cases by isothermal crystallization experiments and extrapolation of the determined T_m to the point were $T_m=T_c$, where T_c is the crystallization temperature[27]. However, even this experimental method is open to question[28]. Also, the high temperature annealing regimes that would be required for the polyamide blends described here could easily compromise the data obtained. As pointed out by Ellis[29] there are difficulties with the application of a Hoffman–Weeks analysis to polyamide blends, namely, very slow crystallization rates and resulting concerns with possible transamidation reactions at high temperatures for long times. Because of these problems, the melting temperatures T°_m and T°_{mb} were measured for materials crystallized for long times at temperatures below the melting temperature.

Figure 14 shows a plot of $(1-T^\circ_{mb}/T^\circ_m)$ *versus* $(1-\phi_2)^2$ for the nylon 46 blend with TFMBPP. T°_{mb} and T°_m were taken as the T_ms obtained after the blends had been annealed as described in the Experimental section. Linear regression yields a straight line with a slope of 0.0825. The molar volumes, $v_1=296.30$ and $v_2=107.15\,\mathrm{cm^3\,mol^{-1}}$, were calculated from the group contributions[30,31]. The molar volume of the trifluoromethyl group ($31\,\mathrm{cm^3\,mol^{-1}}$) was calculated from the recommended values for atomic contributions.

The ΔH_2 for 100% crystalline nylon 46 is not known. The best value available[32] is $35.3\,\mathrm{kJ\,mol^{-1}}$. Using Van Krevelen's[31] tentative values of group contributions to the heat of melting, i.e. $\mathrm{CH_2}=4.0\,\mathrm{kJ\,mol^{-1}}$ and $\mathrm{CONH}=2.0\,\mathrm{kJ\,mol^{-1}}$, a ΔH_2 of $36\,\mathrm{kJ\,mol^{-1}}$ was obtained. The closeness of these two values lends confidence to the use of $35.3\,\mathrm{kJ\,mol^{-1}}$ for the heat of fusion. The value of R is $8.314\,\mathrm{J\,mol^{-1}\,K^{-1}}$ and the temperature is 570 K. Rearrangement of the preceding equations and solution for χ yields a value of -0.0010.

In a similar manner the interaction parameter can be

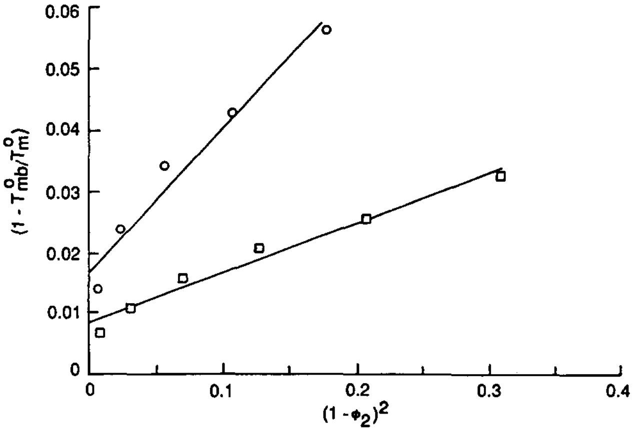


Figure 14 Analysis of the melting point depression of nylon 46/TFMBPP (□) and nylon 6/TFMBPP (○) blends (calculated by equation (4))

calculated for the nylon 6/TFMBPP blends. The molar volume, v_2, is 107.15 cm^3 mol^{-1}, T is 496 K and the slope of the $(1-T^\circ_{\mathrm{mb}}/T^\circ_{\mathrm{m}})$ *versus* $(1-\phi_2)^2$ plot is 0.231 (*Figure 14*). A value of 28.29 kJ mol^{-1} was used for ΔH_2[33]. A value of -0.0044 is found for χ. Both values for χ, -0.0010 and -0.0044, are consistent with the single T_g results and the fact that these are miscible polymer blends.

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