

Critical miscibility limits in blends of aliphatic polyamides containing an aromatic polyamide

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An investigation of the phase behaviour of the aromatic polyamide, nylon 3Me6T, in a specially prepared series of aliphatic copolyamides, $-(CH_2)_n-NHCO-$, has allowed for an unambiguous determination of the critical miscibility limits in these blends. The appearance of critical solution behaviour, in the form of an LCST, in a copolymer of caprolactam and lauro lactam has identified the upper bound for the volume fraction of methylene units of the latter to correlate perfectly with a value estimated previously to be $x = 0.85$. A similar evaluation of blends containing copolymers of 2-pyrrolidinone and caprolactam has determined the lower bound to be $x = 0.76$, which is significantly greater than the estimated value. These observations, when treated within the framework of a mean field binary interaction model, allow for greater precision in projecting the phase behaviour of polyamide blends. The results are also used to corroborate previous findings which describe the phase behaviour of an aromatic polyamide, nylon 6IcoT, in a similar series of aliphatic polyamides.

(Keywords: polyamides; blends; critical miscibility limits; binary interaction model)

INTRODUCTION

Recent communications¹⁻³ have established a foundation from which to formulate a systematic investigation of the structural and chemical factors controlling the phase behaviour of polyamide blends. In essence, these papers detail the application and extension of a mean-field binary interaction model to describe the experimentally observed phase behaviour of aliphatic/aromatic polyamide blends. By considering the polymers in question to be copolymers, composed appropriately of methylene, phenyl and amide functionalities, it was possible to project the phase behaviour of any polyamide blend provided that the components could be rationalized within this scheme. This blueprint for describing polyamide blend phase behaviour, however, contains some crudely focused boundaries which could easily be refined by addressing the deficiencies in the approximations involved in establishing the critical limits necessary for the application of the model. This paper details the experiments conducted to define these limits with greater precision and the application of the improved model to re-examine the phase behaviour of an additional aromatic polyamide, nylon 6IcoT, in blends of aliphatic nylons.

The solubility of nylon 3Me6T in a homologous series of aliphatic polyamides was found to be limited to an upper and lower bound concentration of amide functionalities of the latter^{1,2}. These critical limits are of immense importance since they were used to establish equations from which the segmental interaction parameters, χ_{ij} could be calculated. Additional approximations, including an estimated value of the Flory interaction parameter for the nylon 6/nylon 3Me6T blend, were also required to apply the model. This data point simply represented a scaling factor that, as a first approximation, did not substantially influence the overall

predictive quality of the model. With regard to the critical miscibility limits, however, it was noted that their exact numerical value could not be determined since only a limited number of aliphatic polyamides were available. Accordingly, the upper bound was estimated to be at a volume fraction of methylene units, x , of 0.85 and the lower bound was estimated to be 0.745. These values are approximately intermediate between the ranges of $0.8409 < x < 0.8685$ and $0.7255 < x < 0.7676$, respectively, the values of x for nylons 610 and 612 and nylons 46 and 6, respectively.

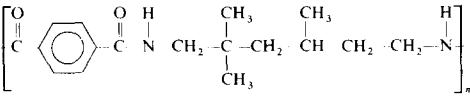
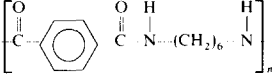
From the foregoing, it should be possible to synthesize polymers with values of x between the two ranges by making copolymers of the required composition using caprolactam and lauro lactam for the upper bound range, and 2-pyrrolidinone and caprolactam for the lower bound range. Synthetic routes to these copolyamides are well documented in the literature⁴. Consequently, it should be possible to obtain a precise measurement of the lower and upper bound values of x by examining the phase behaviour of nylon 3Me6T in suitable copolyamides. This has now been achieved and the results are presented here.

EXPERIMENTAL

Materials

The structure and properties of the aromatic polyamides have been defined previously^{1,2} and a summary is presented in Table 1. Nylon 3Me6T, a condensation product of 2,2,4-trimethyl-1,6-hexanediamine and terephthalic acid, was obtained from Dynamit Nobel (Trogamid T) and nylon 6IcoT, a condensation product of 1,6-hexanediamine and a mixture of isophthalic and terephthalic acids, was obtained from DuPont (Zytel

Table 1 Composition and properties of aromatic polyamides A_yB_zC_{1-y-z}

Polymer	Structure	T _g (°C)	10 ⁻³ M _n	10 ⁻³ M _w	Mer volume fraction ^a		
					Methylene units, y	Amide units, z	Phenyl units 1 - y - z
Nylon 3Me6T ^b		147	20	63	0.5723	0.1915	0.2362
Nylon 6IcoT ^c		127	14	50	0.4702	0.2373	0.2925

^aCalculated using group contribution to molar volume of polymers⁶^bContains exclusively 1,4 phenyl substitution^cContains 1,3 and 1,4 phenyl substitution in the approximate ratio 0.68:0.32**Table 2** Composition and properties of caprolactam/lauro lactam copolyamides (CL/LL)

Monomer feed composition, CL/LL	Polymer composition, CL/LL	10 ⁻⁴ M _n	10 ⁻⁴ M _w	T _g ^a (°C)	T _c ^a (°C)	T _m ^a (°C)	Volume fraction of methylene units ^b , x
60/40	55.6/44.4	28.2	74.8	31	N.o.	N.o.	0.835
55/45	51.2/48.8	24.4	76.8	33	N.o.	N.o.	0.840
50/50	43.8/56.2	28.8	94.7	26	90	124	0.847
40/60	36.0/64.0	20.7	81.7	28	70	132	0.854
32/68	27.7/72.3	18.9	53.4	27	60	137	0.861

^aValues reported for samples quench cooled in liquid nitrogen from the melt. N.o., not observed^bCalculated using group contribution to molar volume of polymers⁶**Table 3** Composition and properties of 2-pyrrolidinone/caprolactam copolyamides (2P/CL)

Monomer feed composition 2P/CL	Polymer composition 2P/CL	10 ⁻³ M _n	10 ⁻³ M _w	T _g ^a (°C)	T _c ^a (°C)	T _m ^a (°C)	Volume fraction of methylene units ^b , x
10/90	6.5/93.5	38.0	117.7	43	74	213	0.763
25/75	12.5/87.5	28.7	76.8	44	84	201	0.758
50/50	17.6/82.4	17.2	39.8	44	114	168	0.754
40/60	24.1/75.9	12.7	23.7	48	101	183	0.749

^aValues reported for samples quench cooled in liquid nitrogen from the melt^bCalculated using group contribution to molar volume of polymers⁶

330). The caprolactam/lauro lactam (CL/LL) copolymers and the 2-pyrrolidinone/caprolactam (2P/CL) copolymers were synthesized by anionic polymerization methods in a manner based upon known procedures⁵.

Caprolactam and lauro lactam (total mass ≈ 100 g) were copolymerized at ≈ 140°C using sodium hydride (NaH) as the initiator and isophorone diisocyanate (IPDI) as the activator in concentrations of approximately 1.2 and 0.8 mol% respectively. The polymerization proceeded rapidly with apparently very high monomer conversion to produce a solid mass, generally in <2 min. The approximate monomer feed ratio for each copolymer is recorded in Table 2. Small portions of each polymer were dissolved in a trifluoroethanol/methylene chloride (3/2 v/v) solvent mixture and precipitated into diethyl ether with vigorous stirring. The purified polymers were then dried in a vacuum oven at ambient conditions (12 h) with an identical final 'drying' cycle at ≈ 80°C. The copolymer with a high lauro lactam content (27.7/72.3) was difficult to dissolve in the trifluoroethanol based solvent and was precipitated into

diethyl ether from hot *m*-cresol solution.

The copolymerization of 2-pyrrolidinone and caprolactam by similar procedures was attempted under a variety of conditions, using different activators. The main problems encountered were poor yields and/or low molecular weight. In addition, the dryness of the two monomers was found to be of critical importance and consequently the successful polymerizations occurred when the 2-pyrrolidinone was distilled from calcium hydride immediately before use.

Three of the copolymers produced, shown in Table 3, were prepared at 140°C using sodium hydride (≈ 3.75 mol%) and hexamethylene diisocyanate (HMDC, ≈ 0.5 mol%) as the activator. An additional copolymer was obtained under similar conditions using 2.3 mol% of sodium hydride and ≈ 0.8 mol% of IPDI as the activator. In all cases the total monomer content in the reaction mixture was ≈ 100 g; the monomer composition is recorded in Table 3. The polymers were subsequently purified by precipitation from the trifluoroethanol solvent in a manner identical to that described above.

Procedures

Blends (50:50 w/w) were prepared by co-precipitation from a common solvent (trifluoroethanol/methylene chloride) into a non-solvent (diethyl ether) using procedures described previously^{1,2}. Thermal analysis was conducted using a Perkin-Elmer differential scanning calorimeter (d.s.c.), Series 7, at a heating rate of 10°C min⁻¹. The glass transition temperature T_g , is recorded as the onset of the transition, and the crystallization peak, T_c , and melting point, T_m , are recorded at the maximum of the respective thermogram peak.

Molecular weight characterization was effected by size exclusion chromatography (g.p.c.) on solutions in *m*-cresol at 110°C using a Waters Associates ALC chromatograph. Values of M_n and M_w were computed using a universal calibration based upon polystyrene standards and, therefore, the values should be viewed for comparison only.

The composition of the purified copolymers was analysed using nuclear magnetic resonance (n.m.r.) methods. The composition of the CL/LL copolymers was determined using proton n.m.r. at 270 MHz on an IBM Industries NR270-AF instrument. The composition of the 2P/CL copolymers was determined by ¹³C n.m.r. at 67.9 MHz with broadband proton decoupling.

RESULTS AND DISCUSSION

The composition and properties of the copolyamides

A summary of the composition and thermal characteristics of the copolyamides, CL/LL and 2P/CL, is presented in Tables 2 and 3, respectively. The molar ratio of the respective monomers in the copolymers was found to be readily available by n.m.r. procedures. From these values, the volume fraction of methylene units for each copolymer could be calculated using values of group contribution to the molar volume polymers⁶. The values of M_n and M_w for the CL/LL copolymers are probably too large owing to a simple calibration based upon polystyrene standards. However, the highly viscous nature of the solutions of these copolymers, observed during their purification, indicates that the anionic mechanism is capable of producing very high molecular weight materials. In contrast to this observation, the 2P/CL copolymers appeared to be relatively low in molecular weight, with a notable low 2-pyrrolidinone content in relation to the monomer feed composition.

These features are in qualitative agreement with previous studies⁷ and confirm the reduced ability of this monomer to polymerize at elevated temperature (140°C). Several polymerizations were done at lower temperatures (110°C) to facilitate the improved polymerizability of the 2-pyrrolidinone monomer under these conditions. However, the yields were seriously depleted since at these temperatures, the polymerizability of the caprolactam becomes substantially reduced. Despite these problems with the 2P/CL polymer preparation, it was possible to produce materials suitable for the determination of the lower bound, as will be described shortly.

The thermal behaviour of the two groups of copolymers is also in approximate agreement with previous work^{8,9} and confirms essentially the random nature of the copolymers¹⁰. In both series of copolymers, the T_g is relatively insensitive to composition, and the crystallization behaviour (T_c) and melting point (T_m) reveal a systematic variation in accordance with their respective composition. Note that the thermal behaviour tabulated is obtained from samples quench cooled from the melt.

Phase behaviour of caprolactam/lauro lactam (CL/LL) copolyamide blends with nylon 3Me6T

In a previous study² it was shown that nylon 3Me6T is completely miscible in nylon 612 ($x = 0.8409$) but immiscible in nylon 11 ($x = 0.8685$). Accordingly, it may be argued that a blend of nylon 3Me6T with a CL/LL copolyamide, possessing a particular value of x between these points, should exhibit critical behaviour, in the form of a lower critical solution temperature (LCST). This has indeed been found to be the case and details are presented below.

The subjective evaluation of calorimetric analysis, coupled with the intricate nature of the thermograms produced by the blends, demands that a pictorial summary be presented, as shown in Figure 1. A quantitative summary of the thermal behaviour of the blends is also provided as Table 4. Thermograms A and B (Figure 1a) of blends where $x = 0.835$ and $x = 0.840$, respectively, clearly demonstrate complete miscibility, whereby the single T_g observed is approximately intermediate between those of their respective pure constituents (see also Table 4). A thermogram of pure CL/LL ($x = 0.835$) is presented as C for comparison. In addition, it has already been shown that nylon 3Me6T has a $T_g \approx 147^\circ\text{C}$ ^{1,2}. The T_g s of the miscible blends were also

Table 4 Summary of the thermal properties and phase behaviour of Nylon 3Me6T/aliphatic polyamide blends

Blend component ^a	Volume fraction of methylene units (x)	T_g^b (°C)	T_c (°C)	Phase behaviour ^c
2P/CL 6.5/93.5 (43)	0.763	77	166	M
2P/CL 12.5/87.5 (44)	0.758	52,108	118	PM
2P/CL 17.6/82.4 (44)	0.754	55,109	N.o. ^d	PM
2P/CL 24.1/75.9 (48)	0.749	52,121	115	PM
CL/LL 55.6/44.4 (31)	0.835	81	N.o.	M
CL/LL 51.2/48.8 (33)	0.840	75	N.o.	M
CL/LL 43.8/56.2 (26)	0.847	70	N.o.	M ^e
CL/LL 36.0/64.0 (28)	0.854	35,125	N.o.	PM
CL/LL 27.7/72.3 (27)	0.861	29,—	75	I

^aNumber in brackets is the pure component T_g

^bNylon 3Me6T has a T_g of 147°C, $\Delta C_p \approx 0.39 \text{ J g}^{-1} \text{ K}^{-1}$

^cM, miscible; I, immiscible; PM, partially miscible

^dN.o., not observed

^eMiscible, but with the appearance of an LCST at $\approx 230^\circ\text{C}$

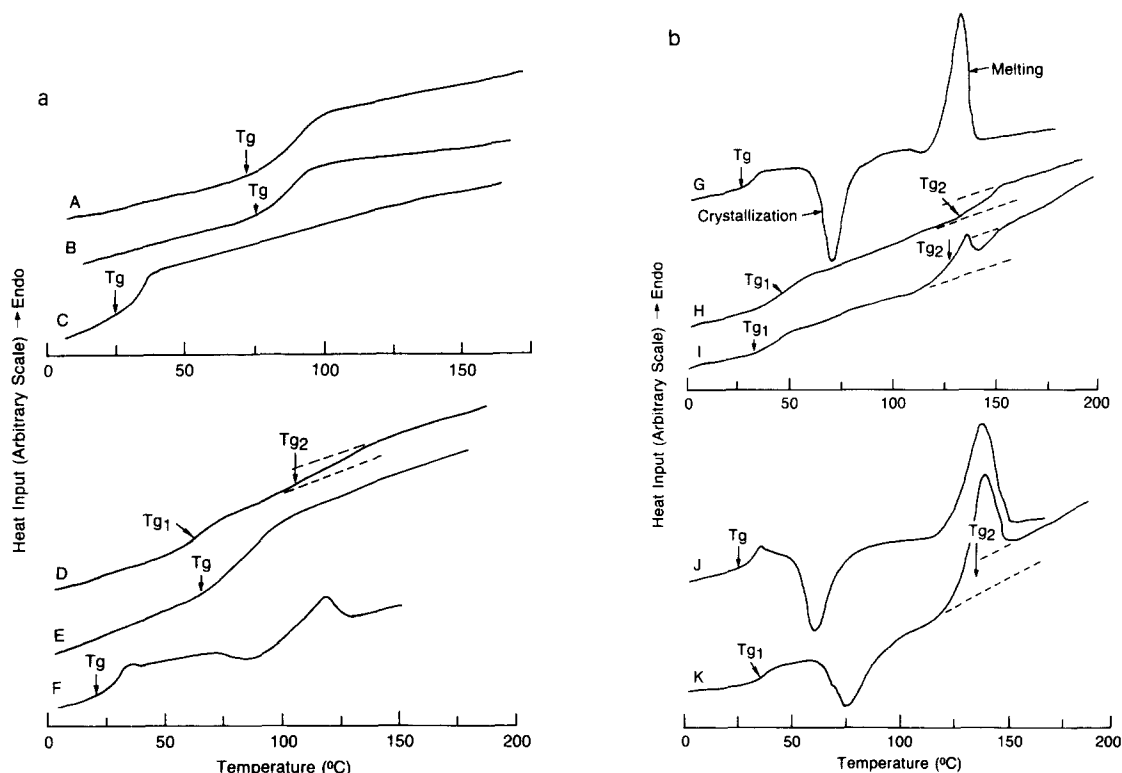


Figure 1 Representative thermograms of caprolactam/lauro lactam copolyamides and their blends with nylon 3Me6T: A, CL/LL ($x = 0.835$)/nylon 3Me6T; B, CL/LL ($x = 0.840$)/nylon 3Me6T; C, CL/LL ($x = 0.835$); D, CL/LL ($x = 0.847$)/nylon 3Me6T, 270°C, 1 min; E, CL/LL ($x = 0.847$)/nylon 3Me6T, 210°C, 15 min; F, CL/LL ($x = 0.847$); G, CL/LL ($x = 0.854$); H, CL/LL ($x = 0.854$)/nylon 3Me6T, 200°C, 15 min; I, CL/LL ($x = 0.854$)/nylon 3Me6T, 250°C, 3 min; J, CL/LL ($x = 0.861$); K, CL/LL ($x = 0.861$)/nylon 3Me6T

found to agree with theoretical predictions¹¹, and measurements of the incremental change of heat capacity, ΔC_p , at T_g of these blends also supported the conclusion of complete miscibility. Note also that thermogram C describes a completely amorphous CL/LL polymer, a feature displayed by one other CL/LL polymer, which also failed to crystallize during analysis (see Table 2). Polymers with a higher lauro lactam content, however, were seen to crystallize during analysis, as noted by a substantial crystallization exotherm and subsequent melting. The two amorphous polymers exhibited a crystalline melting point after annealing, illustrating that the difference in behaviour is attributable to the influence of copolymerization on the crystallization kinetics⁹. This feature will also be of importance when assessing blend phase behaviour, as will be detailed subsequently.

The behaviour described so far is in accord with expectations. The two copolymers have values of x below that of nylon 612 and are therefore within the miscibility range noted earlier. Thermograms D and E in Figure 1a are of a blend containing the CL/LL copolymer where $x = 0.847$, a methylene content greater than that of nylon 612. Thermogram E indicates a completely miscible system. However, after a sample has been exposed to 270°C for 1 min, two T_g s are clearly visible (see thermogram D, and Table 4). Thermogram F for the pure copolymer is provided for comparison. Phase separation in the form of an LCST has taken place at a temperature between 210 and 270°C. Although not shown, a thermogram of a sample exposed to 230°C appears to mark the point at which phase separation occurs.

Thermograms G, H and I shown in Figure 1b exemplify

the behaviour of the blend containing the CL/LL copolymer where $x = 0.854$ and again illustrate the inherent crystallizability of this particular copolymer which, although missing in thermogram H, is present in thermogram I. This is observable as a crystalline melting superimposed on a ΔC_p change at the T_g of the nylon 3Me6T rich phase after the blend has been exposed to a higher temperature (250°C, 3 min). Evidently, the improved phase separation on exposure to the higher temperature allows for the aliphatic nylon rich phase to crystallize to a sufficient extent on cooling for a melting endotherm to be observed during heating.

The behaviour described above is more clearly observable on inspection of the blend where $x = 0.861$, thermograms J and K in Figure 1b. The blend is almost completely immiscible, as noted by the T_g of the aliphatic polyamide rich phase (see Table 4), which is very close to that observed for the pure aliphatic polyamide. The nylon 3Me6T rich phase has a T_g which again is not readily observable, but its value appears to be close to that for the pure polymer. Further experimental evidence supporting the conclusion of virtually complete immiscibility is provided by inspection of the crystallization exotherm in the blend, which is only marginally affected ($T_c = 75^\circ\text{C}$), compared to the pure copolymer ($T_c = 60^\circ\text{C}$). One would expect this thermal event to be greatly influenced by the addition of the non-crystallizable diluent, provided that it was present in substantial

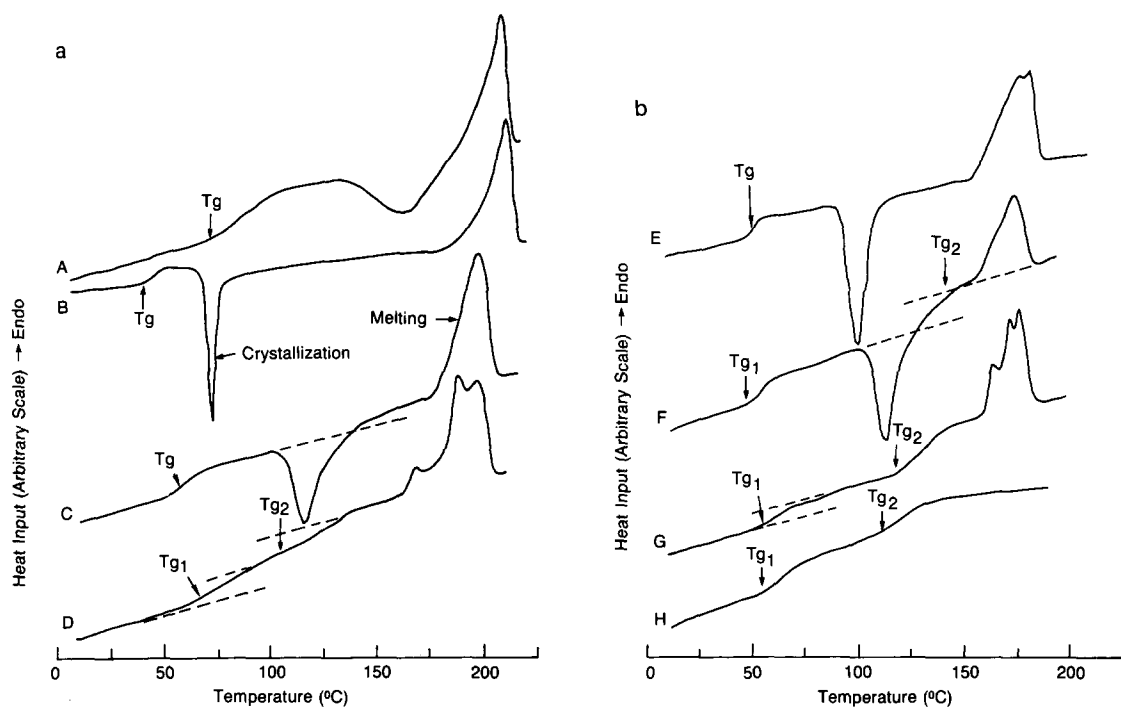


Figure 2 Representative thermograms of 2-pyrrolidinone/caprolactam copolyamides and their blends with nylon 3Me6T. A, 2P/CL ($x = 0.763$)/nylon 3Me6T; B, 2P/CL ($x = 0.763$); C, 2P/CL ($x = 0.758$)/nylon 3Me6T; D, 2P/CL ($x = 0.758$)/nylon 3Me6T, 160°C, 15 min; E, 2P/CL ($x = 0.749$); F, 2P/CL ($x = 0.749$)/nylon 3Me6T; G, 2P/CL ($x = 0.749$)/nylon 3Me6T, 155°C, 60 min; H, 2P/CL ($x = 0.754$)/nylon 3Me6T

quantity. The decisive behaviour of the CL/LL copolymer, where $x = 0.861$ (cf. nylon 11 where $x = 0.8685$), indicated that blend studies involving copolyamides with larger values of x were unnecessary.

From the foregoing discussion, and the observation of an LCST at 230°C for the copolymer where $x = 0.847$, it is possible to infer that the upper bound for miscibility within these blends occurs at $x = 0.85$. This value agrees perfectly with that obtained by indirect methods².

Phase behaviour of 2-pyrrolidinone/caprolactam (2P/CL) copolyamide blends with nylon 3Me6T

Using the same criteria of examining the value of T_g , the quantity ΔC_p at T_g and the influence of adding nylon 3Me6T to the crystallization exotherm of the pure copolymer, the phase behaviour of blends of 2P/CL containing nylon 3Me6T was evaluated in an identical manner to that described above. Thermograms A and B in Figure 2a illustrate the complete miscibility of 2P/CL, $x = 0.76$, in nylon 3Me6T. A quantitative summary of the observed behaviour is also presented in Table 4. Thermograms C and D in Figure 2a demonstrate the partial miscibility of the blend containing 2P/CL when $x = 0.758$. The quench cooled blend contains an aliphatic polyamide rich phase where $T_g \approx 52^\circ\text{C}$, a value only slightly above that of the pure polymer ($T_g = 44^\circ\text{C}$). In addition, the crystallization exotherm has moved to a significantly higher temperature ($T_c = 118^\circ\text{C}$) than the pure copolyamide ($T_c = 84^\circ\text{C}$). This is an expected consequence of adding a miscible higher T_g amorphous polymer to a lower T_g crystallizable polymer. The T_g of the nylon 3Me6T rich phase is only visible when the blend has been annealed, as shown in thermogram D.

The thermal behaviour of the blend when the methylene unit content has been decreased further ($x = 0.749$) is also consistent with only partial miscibility, as shown

in Figure 2b (thermograms E, F and G) and Table 4. However, it is worth emphasizing that the observed partial miscibility is almost certainly attributable to the lower molecular weight of this copolymer. The hidden T_g of the nylon 3Me6T rich phase in thermogram F is again fully exposed by annealing, as shown in thermogram G. Thermogram H, also shown in Figure 2b, of the blend containing the 2P/CL copolymer where $x = 0.754$, displays behaviour consistent with a partially miscible blend (see also Table 3).

From these observations, it can be concluded that the most probable value for the lower bound of miscibility in these blends is $x = 0.76$. The appearance of partial miscibility in the blends when x is below this limit is almost certainly entropic in origin due to the low molecular weight of these polymers compared to the CL/LL copolymers.

Impact of copolyamide/nylon 3Me6T blend phase behaviour on the binary interaction model

Previous communications^{1,2} presented a detailed framework for a predictive model to account for the phase behaviour of aliphatic/aromatic polyamide blends. Only the essential details will be repeated here as they are relevant to the discussion. Provided the polymers in question can be rationalized in terms of the functionalities A, B and C, which represent methylene, amide and phenyl groups, respectively, then routine Flory-Huggins polymer-polymer solution thermodynamics can be used to define an effective interaction parameter, χ_{blend} . If χ_{blend} is calculated to be negative, then miscibility should be expected. By assuming that the methyl groups of the hydrocarbon component of nylon 3Me6T interact in an identical manner to methylene units, it has been demonstrated that for blends defined as $A_x B_{1-x} / A_y B_z C_{1-y-z}$ copolymers, where $A_x B_{1-x}$ represents the aliphatic

polyamide and $A_yB_zC_{1-y-z}$ represents the aromatic polyamide, χ_{blend} can be formulated as²:

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

The χ_{crit} term arises from entropic considerations and as a first approximation can be neglected. Thus in the general situation, for high molar mass polymers, χ_{blend} equates with the first three terms of equation (1) such that $\chi_{\text{blend}} > 0$ signifies immiscibility and $\chi_{\text{blend}} < 0$ signifies miscibility. From this reasoning, it follows that a general solution to the above equation, and hence χ_{blend} , can be found by solving numerically for the three segmental interaction parameters χ_{AB} , χ_{BC} and χ_{AC} . Two of the equations necessary to achieve this are obtained by defining $\chi_{\text{blend}} = 0$ at the two critical miscibility limits where blends of aliphatic polyamides containing nylon 3Me6T are transformed from a miscible to an immiscible condition. In earlier calculations² these limits had been estimated as $x = 0.85$ and $x = 0.745$, respectively. However, from the foregoing discussion the limits have now been defined precisely and independently as 0.85 and 0.76, respectively.

The third equation, containing the necessary non-zero value of χ_{blend} , has been defined using the assumed value of $\chi_{\text{blend}} = -0.005$ for the nylon 6/nylon 3Me6T blend². Note that the assumed value of χ_{blend} for nylon 6/nylon 3Me6T acts as a scaling factor and its exact value would only become important in cases where χ_{blend} approaches zero for a particular blend and the χ_{crit} term also assumes a significant role. This situation has been seen to occur, as noted earlier, where blends containing the low molecular weight 2P/CL copolyamides were partially miscible even though their respective values of x were outside the critical limit. With this procedure, values of $\chi_{AB} = 7.982$, $\chi_{BC} = 7.460$ and $\chi_{AC} = -0.288$ have been obtained. These new values are slightly greater than those calculated originally ($\chi_{AB} = 2.685$, $\chi_{BC} = 2.308$, $\chi_{AC} = -0.127$), but when substituted into the appropriate expressions they would still render exothermic heats of mixing of a magnitude considered usual for miscible polymer pairs ($< 0.5 \text{ cal cm}^{-3}$)*.

Using this new information, a summary of the calculated values of χ_{blend} for all the copolyamide blends containing nylon 3Me6T is shown as Figure 3. One interesting feature is worthy of mention. Previous studies², based on experiments designed to measure the depression of melting point in blends of nylon 6 and nylon 3Me6T, had suggested that χ_{blend} for this blend would be very small. This speculation has now been validated to some extent by the experimental evidence provided here, indicating that the lower bound for miscibility occurs at $x = 0.76$, a value which departs only slightly from that of nylon 6 ($x = 0.7676$). A complete summary of the phase behaviour, in the form of χ_{blend} , of nylon 3Me6T in aliphatic polyamides is shown in Figure 4, which also shows the estimated behaviour², for comparison. As can be seen, the overall adjustment from the estimated behaviour is quite minor. The minimum of the curve can be seen to decrease to more negative values of χ_{blend} , but this is simply because of the effect of

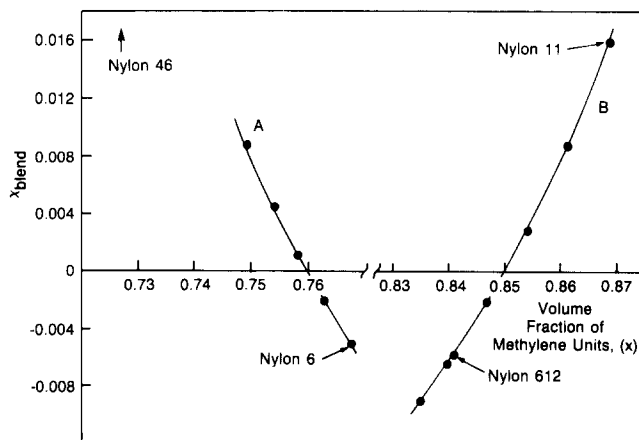


Figure 3 Calculated values of χ_{blend} for blends of copolyamides and nylon 3Me6T: A, 2-pyrrolidinone/caprolactam; B, caprolactam/lauro-lactam

the scaling properties of the χ_{blend} value of the nylon 6/nylon 3Me6T blend, which has been kept constant.

The preceding discussion is essentially consistent with previous findings and represents only a refinement of the quantitative description of the model. Many of the more general predictions² of polyamide blend phase behaviour remain largely unchanged, but the detailed experimental behaviour of blends of nylon 6IcoT will be reviewed in the light of the new findings described here. Nylon 6IcoT is an aromatic polyamide containing a mixture of phenyl isomers. By assuming that the interaction of this mer is relatively unaffected by this structural variable then this polymer may also be treated in an identical manner to nylon 3Me6T. It has been reported previously that blends of nylon 6IcoT containing nylon 4, 610 and 612, respectively, are immiscible and blends containing nylons 46, 6, 66 and 69 are miscible². These observations are still in perfect agreement with calculations using the new segmental interaction parameters, as shown in Figure 4. Again, the estimated behaviour is shown for comparison. The blends containing nylon 46 up to nylon 69 are predicted to be miscible and the blend containing nylon 610 is above its respective critical value ($x \approx 0.814$) and is, therefore, immiscible. An additional experimental observation in support of the calculated behaviour for this polymer was obtained by inspection of the phase behaviour of a blend of nylon 6IcoT containing 2P/CL ($x = 0.754$). As mentioned previously, a blend of this polymer with nylon 3Me6T was found to be immiscible, but the blend with nylon 6IcoT is predicted to be miscible ($\chi_{\text{blend}} = -0.0246$). Thermal analysis of the latter blend revealed a single T_g at 70°C, in approximate agreement with a result based on theoretical calculations¹¹ and, therefore, conclusive evidence of complete miscibility.

CONCLUSIONS

An examination of the phase behaviour of an aromatic polyamide, nylon 3Me6T, in a series of aliphatic copolyamides has established the critical miscibility limits for the volume fraction of methylene units of the latter to be 0.76 and 0.85, respectively. These values, when incorporated into a mean-field binary interaction model, result in an improved definition of the model boundaries over those proposed previously for these particular blends. In keeping with the simplicity of this type of group

* 1 cal = 4.184 J

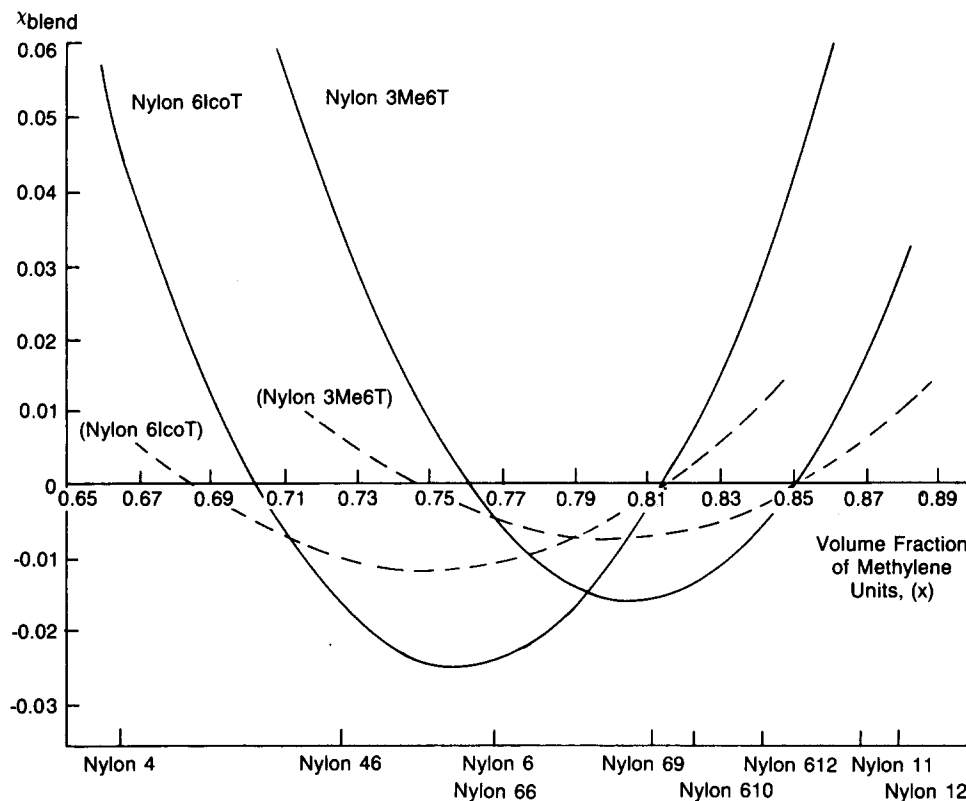


Figure 4 Calculated values of χ_{blend} for $A_xB_{1-x}/A_yB_zC_{1-y-z}$ polyamide blends; ---, estimated values from Reference 2

contribution approach to describe polymer blend phase behaviour, this refinement has not required any conceptual or philosophical adjustments. In addition, a re-examination of the known phase behaviour of nylon 6IcoT, with respect to these new results, has proven to be reassuringly uneventful compared to previous projections.

The results presented here also provide further experimental vindication of a binary interaction model to describe polyamide blend phase behaviour without resorting to the inclusion of specific interactions in the form of amide–amide hydrogen bonding interactions. Consequently, it may be argued that the average state of hydrogen bonding in the pure components and in the blend remains essentially unchanged. In addition, the uniformity of phase behaviour in the copolyamide blends implies that the sequence of amide units is relatively unimportant. In other words, nylon 11 behaves in an identical manner to a nylon 6/nylon 12 copolymer containing the same proportion of amide units. This is not surprising since there are no diad or triad sequences of this functionality. The use of an assumed value of the interaction parameter for the nylon 6/nylon 3Me6T blend still represents a minor blemish on the quantitative aspects of the application of the model. For the blends described here this approximation is of little consequence. However, a methodology to quantify completely all aspects of the model, by determining a non-zero value of the interaction parameter for a particular

blend, is currently under consideration. The application of these concepts to blends of additional aromatic polyamides of much greater chemical complexity is currently under study and will form the subject of a future communication.

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REFERENCES

- 1 Ellis, T. S. *Polymer* 1988, **29**, 2015
- 2 Ellis, T. S. *Macromolecules* 1989, **22**, 742
- 3 Ellis, T. S. in 'Multiphase Macromolecular Systems' (Ed. B. M. Culbertson), Plenum Press, New York, 1990, p. 411
- 4 Sekiguchi, H. 'Ring-Opening Polymerization', (Eds K. J. Ivin and T. Saegusa), Elsevier, New York, 1984, Vol. 2, pp. 809–919
- 5 Garner, D. P. and Fasulo, P. D. *J. Appl. Polym. Sci.* 1988, **36**, 495
- 6 Van Krevelen, D. W. 'Properties of Polymers', Elsevier, New York, 1976
- 7 Schrawski, G. *Makromol. Chem.* 1972, **161**, 69
- 8 Goodman, I. and Kehayoglou, A. H. *Eur. Polym. J.* 1983, **19**, 321
- 9 Kobayashi, F. and Matsuya, K. *J. Polym. Sci.* 1963, **A1**, 111
- 10 Kricheldorf, H. R. and Hull, W. E. *J. Polym. Sci., Polym. Chem. Edn* 1978, **16**, 2253
- 11 Couchman, P. R. *Macromolecules* 1978, **11**, 1156