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Miscibility of polyamide blends: effects of configuration

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The influence of the configuration of elementary chemical species, such as methylene, amide and phenyl groups, upon the phase behaviour of polyamide blends has been examined with reference to poly(hexamethylene isophthalamide), (nylon-6I) and poly(*m*-xylene adipamide) (MXD6), respectively, in aliphatic polyamides. The observable differences have been correlated with a binary interaction model to illustrate how the segmental interaction parameters are affected. It is proposed that the small differences detected may be attributed to the influence of neighbouring species on the interactions and that segments should be considered in terms of their triad groups. This is analogous to the approach already applied to blends of random addition copolymers. Additional experimental investigations, accompanied by predictive calculations, are also presented for blends of MXD6 with various aromatic polyamides, including the aramid poly(*m*-phenylene isophthalamide), and various aliphatic copoly(ester–amides).

(Keywords: polyamide blends; configuration; interactions)

INTRODUCTION

The optional blending or alloying of polymers is a relatively simple route for developing new improved materials. In order to perform this effectively, a fundamental understanding of the mixing behaviour of the polymers involved will be helpful for formulating useful materials. With the latter in mind, considerable expertise has been developed[1–6] for blends based upon aliphatic and aromatic polyamides. The experimentally observed behaviour has been correlated with a binary interaction model[7–9] to demonstrate that the relationship between chemical structure and polymer–polymer solubility is often a simple one. These studies have also been able to show semi quantitatively how minor variations of chemical structure, such as isomerism of the phenyl group in aromatic nylons, can be incorporated into the model[4]. Although these discussions provide a broad picture for describing the phase behaviour of polyamide blends, which is consistent with theory, there are a number of deficiencies to the approach developed thus far which are related to an inability to account for differences of configuration of polymer segments, i.e. the sequential arrangement of chemical species.

In this paper, the mixing behaviour of poly(*m*-xylene adipamide), (MXD6), will be compared to that of a configurational variant of MXD6, i.e. nylon-6I (poly (hexamethylene isophthalamide)), in a number of different situations.

Recent studies[4,10,11] of blends based on MXD6 and aliphatic polyamides have already noted distinguishable mixing behaviour, when compared with nylon-6I, even though they contain the same chemical species in exactly the same proportions. Formulating the model upon a simple nomenclature founded upon the elementary chemical species, i.e. methylene, amide, and phenyl, fails to account for this different behaviour[3]. This result is not surprising and indeed should be expected from an approach which fails to include the influence of neighbouring groups upon segmental interactions. The influence can be entropic, enthalpic or both; however, the question of configuration in the context of polymer interactions has been addressed on a number of occasions with reference to sequence distributions in random addition copolymers[12–16]. The same ideas can in principle be applied to polyamides, and the purpose of this communication is to incorporate some of these features into the analysis of polyamide blends. This is important for two reasons. First, it allows an improved understanding of how sequence effects in polymer molecules influence the mixing behaviour. Of more immediate interest, however, is the fact that the information may be applied to quantify the mixing behaviour of polyamide–polyester blends. Recent studies[17,18] have documented an extension of the predictive model to describe mixing of aliphatic polyamide–polyester blends. In order to include polyesters with aromaticity, e.g. poly (butylene terephthalate) (PBT), sequence effects, such as placing ester groups adjacent to phenyl groups, will have to be considered. It is anticipated that the information developed here will also assist towards this objective.

EXPERIMENTAL

Materials

Details of the composition and properties of the aliphatic polyamides and copolyamides have been presented previously[2,4]. A thorough description of many of the aromatic polyamides has also been

Table 1 Structure and properties of aromatic nylon polymers

Polymer	Structure	Glass transition Temperature (°C)	Melting point (°C)
MXD6	$-[(CH_2)_4-CO-NH-CH_2-C_6H_4-CH_2-NH-CO]_n$	83	238
MPI	$-[HN-C_6H_4-NHCO-C_6H_4-CO-]_n$	273	>350
Nylon 6/6T[a]	$-[CO-C_6H_4-CONH(CH_2)_6-NH]_a-[CO(CH_2)_5-NH]_b$	105	297

[a] The ratio $a:b$ is approximately 0.7:0.3 in a random configuration

described in the literature[1-4]; these include nylon-6I (Nydur T40, Bayer), nylon-6I/T (Selar 3426, DuPont), nylon-3Me6T (Trogamid T, Huls), and nylon-12IA (Grilamid TR55, Emser). A summary of the aromatic polyamides investigated here, which have not been introduced in earlier communications, is given in *Table 1*. MXD6 (Toyobo Co. Ltd) is poly(*m*-xylene adipamide) and nylon-6/6T (Ultramid T BASF) has been shown by n.m.r. spectroscopy to be a random copolymer formed by the reaction of 1,6-hexanediamine, caprolactam and terephthalic acid (H, C, T, respectively) in the approximate molar ratio 35:30:35. The aramid polymer, MPI (poly *m*-phenyleneisophthalamide) was obtained as a continuous filament from Du Pont (Nomex®).

Blending

All components were blended in equal proportions (50:50 wt/wt) by precipitation from a common solvent. Blends based upon MPI and nylon 6/6T required concentrated sulfuric acid/water as the solvent/precipitant medium. A large excess of water was used with exhaustive washing. Trifluoroethanol/chloroform (3:2 vol/vol) was used as a solvent for blends containing MXD6, with diethyl ether as the precipitating medium. All of the pure components were subjected to the same preparative procedures as those used for the blends. All materials were dried in a vacuum oven for 24 h, using elevated temperatures (70–80°C) for the final drying period of 6 h.

Characterization and analysis

Thermal analysis was performed by using a Perkin Elmer Series 7 differential scanning calorimeter at a heating rate of 10°C min^{-1}. However, a rate of 20°C min^{-1} was used for enthalpy recovery measurements[19], and for all blends based upon MPI. Blends involving crystallizable polymers were exposed to a temperature just above the respective melting point (T_m) to ensure liquid–liquid equilibrium, and were then quench cooled in liquid nitrogen prior to analysis. The time of exposure was kept to a minimum (~ 1 min).

The criterion of a single glass transition temperature (T_g), intermediate between those of the two pure constituents, was used as a determinant for miscibility. A significant shift of two T_g values, towards an intermediate value, was used as an indication of partial miscibility.

RESULTS AND DISCUSSION

Blends containing nylon MXD6

Aliphatic polyamides. Previous work[10,11] has indicated that nylon-6/MXD6 blends are partially miscible. Exposure of the blends to moderately high temperatures (290°C) for a short period (2–5 min) yields homogeneous mixtures after a minimal degree of transreaction. The thermograms shown in *Figure 1* illustrate the T_g behaviour of MXD6 (A) and the blend with nylon-6 (B) prior to transreaction. Exposure of the blend to 320°C for only 1 min produces a thermogram indicative of a change to a homogeneous blend. These results duplicate earlier findings and serve to illustrate the need to exercise care during interpretation of phase behaviour in these systems. Thermograms C and D in *Figure 1* confirm the multiphase behaviour of blends containing nylon-4 and nylon-612, respectively. Although it is not completely clear from thermogram C that two T_gs are present, enthalpy recovery studies (not shown here) indicate a multiphase system. Exposure of the latter blend to 290°C for 5 min fails to induce any significant homogenization, a result which is also consistent with earlier work[10,11], and signifies a pronounced phase separation with a more unfavourable interaction

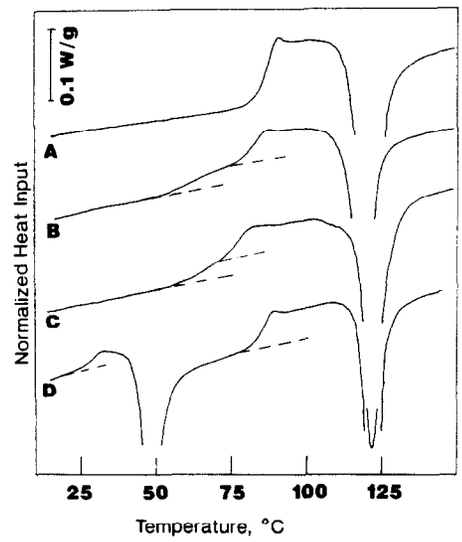

Figure 1 Representative thermograms of blends containing MXD6: (A) pure MXD6; (B) nylon-6; (C) nylon-4; (D) nylon-612

Table 2 Phase behaviour and thermal properties of blends containing MXD6[a]

Blend component[b]	Volume fraction of methylene groups	T_g (°C)	Phase behaviour[c]
Aliphatic polyamides			
Nylon-4 (59)	0.6646	59, 75	I
Nylon-46 (58)	0.7255	73 –	(I/PM?)
2P/CL copolyamide (48)	0.7490	56, –	PM
2P/CL copolyamide (43)	0.7630	52, 80	PM
Nylon-6 (41)	0.7676	52, 78	PM
Nylon-66 (45)	0.7676	51, 77	PM
Nylon-612 (30)	0.8409	28, 82	I
Aromatic polyamides			
Nylon-6I (118)	0.4702	84, 117	I
Nylon-6I/T (123)	0.4702	84, 116	I
Nylon-3Me6T (147)	0.5723	84, 148	I
Nylon-12IA (154)	0.7514	84, 156	I
Nylon-6/6T (105)	0.5236	84, (95)	I

[a] T_g of MXD6 is 83°C
[b] Figures in parentheses are the T_g values of the pure components (°C)
[c] M, miscible; I, immiscible; PM, partially miscible

between the two components than that observed for the blend with nylon-6. High-temperature experiments with nylon-4/MXD6 blends were not performed because of spontaneous depolymerization of nylon-4 above T_m. A summary of the observations noted above is given in *Table 2*.

Thermal investigations of blends of nylon-46, nylon-66 and copolyamides with compositions (i.e. methylene content) intermediate between the latter are also summarized in *Table 2*, with the results shown in *Figure 2*. The blend containing nylon-46 required exposure to 305°C for 1 min to establish a liquid equilibrium. Analysis of the resultant mixture provided the thermogram A which appears to indicate a one-phase system. Enthalpy recovery studies have provided no evidence whatsoever that heterogeneous behaviour is present. Unfortunately, it is difficult to conclude whether this is the result of pure thermodynamic miscibility or transreaction-induced miscibility, since as noted above, a similar thermal exposure of the blend containing nylon-6 also leads to a single T_g. It was not possible to vitrify the blend by quench cooling from the melt. This observation supports the inference of a heterogeneous mixture since miscibility would tend to have a retarding effect on the rate of crystallization. Nylon-66 was found to behave in an identical manner to that of nylon-6 and supports previous assertions[1-4] that from a thermodynamic point of view, nylon-6 and nylon-66 possess indistinguishable mixing behaviour when blended with other polymers. Thermograms B and C illustrate partial miscibility in the pristine state (B), which is transformed to a transreacted blend on exposure to elevated temperatures (thermogram C).

Blends containing copolyamides with $x = 0.749$ and 0.763 (x is the volume fraction of methylene groups) also reveal partial miscibility (thermograms D and E; E was recorded at 20°C min^{-1}, and is not to the same scale as A–D). Careful inspection of the thermogram D reveals a non-uniform T_g which is not readily apparent from *Figure 2*; however, the heterogeneous nature of the crystallization exotherm is easily visible. These results are also recorded in *Table 2*.

From the observations noted above, it is possible to conclude that MXD6 is extremely close to thermodynamic miscibility in aliphatic polyamides and copolyamides of approximate composition $0.72 < x < 0.77$. These observations contrast with those of nylon-6I, the configurational variant of nylon MXD6, which possesses a window of complete miscibility, given approximately by $0.71 < x < 0.81$[4,20]. A quantitative analysis of these observations will be presented in a later section.

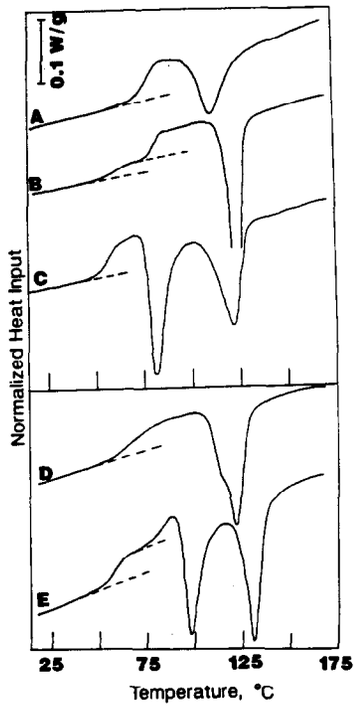

Figure 2 Representative thermograms of blends containing MXD6: (A) Nylon-46; (B) nylon-66; (C) nylon-66 (290°C/3 min); (D) copolyamide, $x = 0.749$; (E) copolyamide, $x = 0.763$.

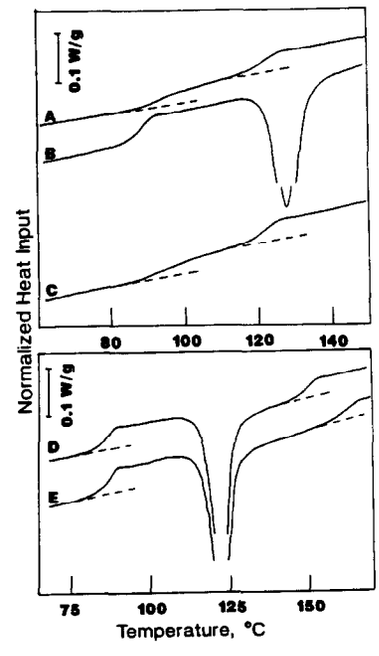

Figure 3 Representative thermograms of blends containing MXD6: (A) nylon-6I/T (crystallized); (B) nylon-6I/T (amorphous); (C) nylon-6I (crystallized); (D) nylon-3Me6T; (E) nylon-12IA

Aromatic polyamides. Blend studies with aromatic polyamides derived from benzene dicarboxylic acids and aliphatic diamines, have indicated, exclusively, the formation of heterogeneous blends. A summary of the results from these studies is shown in *Table 2*, together with a selection of thermograms in *Figure 3*. Thermograms A and B of the blend containing nylon-6I/T, contrast the behaviour of the crystallized and vitrified blend. The glass transition of the nylon-6I/T is only visible after crystallization. An identical situation has been noted for the blend containing nylon-6I (thermogram C) which illustrates that the presence of only 1,3-, or a mixture of 1,3- and 1,4-phenyl isomers in the aromatic polyamide appears to cause little difference. Increasing the effective methylene content of the aromatic polyamide[4] (nylon-3Me6T and nylon-12IA) still results in heterogeneous mixtures, as can be seen in the thermograms D and E.

A blend of MXD6 and nylon-6/6T has been found to give heterogeneous behaviour, but only after a very short exposure to the melt temperature of the latter (320°C). Exposure for 1 min at 330°C appears to give rise to rapid transreaction and the formation of a homogeneous system. Thermograms which illustrate the above conclusions are shown in *Figure 4*. Thermogram B exhibits two T_gs which rapidly merge to a single transition (thermogram C) at a value (88°C) well below that expected for a miscible blend (cf. with thermogram A). Transreaction involving MXD6 at elevated temperatures is also an observable feature of blend studies with aliphatic polyamides (as noted previously). The thermogram D in *Figure 4* may be compared with thermogram B in *Figure 3*. Although complete homogenization has not yet occurred, there has been considerable merging of the two T_gs, closer to a single transition.

Poly (m-phenyleneisophthalamide) (MPI). A previous study[21] of blends of MPI with a homologous series of aromatic polyamides, formed from the condensation of benzene-1, 3-dicarboxylic acid and the respective linear aliphatic diamine $(-CH_2-)_n$ where $n = 3$–9, has indicated a window of miscibility which is given approximately by $n = 6$–7. Partial miscibility was reported when $n = 8$–9. These results describe a window of miscibility for the aromatic polyamides with a methylene content of approximately $0.47 < x < 0.57$. The observations noted in *Table 3*, and shown in *Figure 5*, confirm some of the inferences noted above. Nylon-6I and nylon-6I/T were found to be completely miscible (thermograms C and D); however, nylon-3Me6T was found to be immiscible (thermogram B). If nylon-3Me6T is assumed to belong to the same class of aromatic polyamides, whereby the alkyl fragment is rationalized as a collection of methylene groups, then the latter observation is also consistent with earlier findings[21]. On this basis, the methylene content of nylon-3Me6T (0.5723) is outside the expected region of miscibility (0.5711 for $n = 9$). Once again, the effect of phenyl group isomerism appears to be of little consequence.

The blend of MPI with MXD6 provided behaviour consistent with the formation of a miscible system. The blend T_g (142°C) is less than that expected (159°C) for a miscible blend; however, this may be symptomatic of transition broadening. This particular blend (thermogram E) was exposed to 260°C for 1 min, and it is therefore assumed that the single T_g has not been produced as a result of transreaction. The thermogram shows a crystallization exotherm for the MPI and although not shown, a melting endotherm, mingled

Table 3 Phase behaviour and thermal properties of blends containing MPI

Blend component[a]	T_g (°C)	Phase behaviour[b]
Nylon-6I (118)	166	M
Nylon-3Me6T (149)	151, 252	I
Nylon-6I/T (123)	173	M
MXD6 (83)	142	M
Nylon-6/6T (105)	167	M

[a] Figures in parentheses are the T_g values of the pure components (°C)
[b] M, miscible; I, immiscible

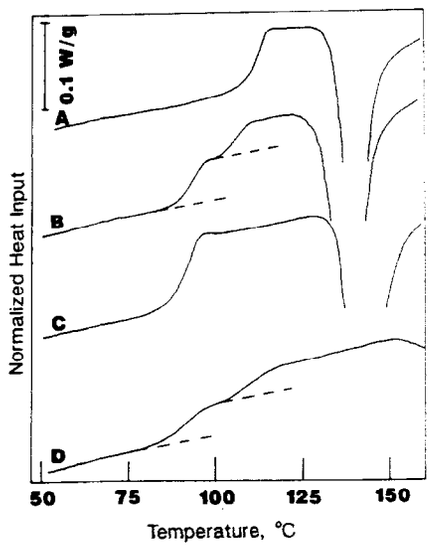

Figure 4 Representative thermograms of blends containing Ultramid T (nylon-6/6T): (A) pure nylon-6/6T; (B) MXD6; (C) MXD6 (330°C/1 min); (D) blend of MXD6/nylon-6I (320°C/1 min)

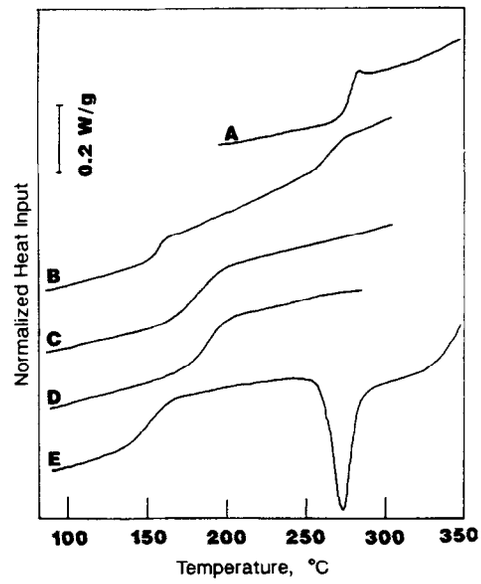

Figure 5 Representative thermograms of blends containing MPI:(A) pure MPI; (B) nylon-3Me6T; (C) nylon-6I; (D) nylon-6I/T; (E) MXD6

with a degradation endotherm, was observed at ~ 390°C. The blend of MPI/nylon-6/6T also indicated the formation of a miscible system.

Theoretical background

Previous communications[1–9] have documented how a Flory–Huggins lattice model for the free energy of mixing, ΔG, includes an enthalpy contribution which can be equated in terms of an effective interaction parameter, χ_{Blend}. The latter occupies the same role as the classical Flory–Huggins χ, where as a first approximation miscibility ensues if $\chi_{\text{Blend}} < 0$. However, as noted in recent publications[17,18], the combinatorial entropy of mixing can have a decisive influence in controlling the phase behaviour in polymers possessing only a moderate molar mass. In reality, χ_{Blend} is really a free energy parameter containing enthalpic and entropic components.

For a mixture of polymers (1,2) containing differing segments (i, j) of volume fraction Ψ, χ_{Blend} may be represented in a simplified form (equation (1)) as an algebraic sum of the inter- and intramolecular interactions:

$$\chi_{\text{Blend}} = \sum_{i,j} \Psi_i^1 \Psi_j^2 \chi_{ij} - \left(\sum_{i,j} \Psi_i^1 \Psi_j^1 \chi_{ij} + \sum_{i,j} \Psi_i^2 \Psi_j^2 \chi_{ij} \right) \quad (1)$$

where χ_{ij} are the segmental interaction parameters, and if all are known, then χ_{Blend} may be calculated and used to define the mixing behaviour. When applied to aliphatic polyamides and copolyamides A_xB_{1-x} (containing methylene (A) and amide (B) segments) in blends of aromatic polyamides (formed from benzene dicarboxylic acids) it has been shown that the most appropriate nomenclature for the latter is A_yC_{1-y} copolymers, where C = NHCO–Ph–CONH. This is necessary because a comparison of the mixing behaviour of nylon-6I and MXD6, polymers which contain exactly the same segments and in the same proportion but arranged in a different configuration or sequence, has shown that the model is not able to distinguish between them if both are classed in the general form as ABC copolymers, where C represents a single phenyl group.

The question of configuration or sequence distributions as an influence on the phase behaviour of polymer mixtures has been frequently studied[8–12]. Consequently, the fact that the mixing behaviour of nylon-6I and MXD6 are different is not surprising if the polymers are examined in terms of their respective segment triads, i.e. if the respective neighbours of the segments are taken into consideration. The aliphatic polyamides contain only AAA, AAB and ABA triads. Regular polyamides from nylon-4 ($x = 0.6646$) to nylon-12 ($x = 0.879$), and copolyamides within this range of x contain only these triads. This explains why the macroscopic configuration difference between nylon-69 and its equivalent, synthesized from the appropriate mixture of a C(6) and a C(12) lactam, has very little effect on the mixing behaviour; on a microstructural scale they contain the same types of triads. Nylon-6I contains AAA, ABC, AAB and BCB triads, whereas MXD6 contains AAA, AAB, ABA, BAC and ACA triads. A tabulation (see *Table 4*) of the various interactions reveals that in blends with aliphatic polyamides only two pairs of interactions are common to both polymers. An examination on this level also reveals that eight and seven parameters are required to estimate χ_{Blend} for nylon-6I and MXD6, respectively. Although more detailed in its description, and therefore potentially more accurate, currently there is insufficient information to estimate all of the χ_{ij} parameters involved.

Blends of MXD6 and aliphatic polyamides. From a practical perspective the situation is not as hopeless as that inferred above. For example, if all of the different kinds of methylene interactions are assumed to be equal (AAA = AAB = BAC), a suitable approximation can be made. Therefore, by defining MXD6 as $A_rB_sC^*_{1-r-s}$ (C* represents an isolated phenyl group but is not the same as that present in nylon-6I) and using an independent value of $\chi_{AB} = 8.534$[17] the observations reported in *Table 4* may be fitted to the model. The results, although empirical, are shown in *Figure 6* and the parameters χ_{BC^*} and χ_{AC^*} that are obtained are shown in *Table 5*. It should be noted that only minor adjustments of the latter parameters lead to very unrealistic values of χ_{Blend} when compared to the experimentally observed behaviour. Moreover, the small value for χ_{AC^*} (0.1) is essential in order to give a value of χ_{Blend} for MXD6 in nylon-6 (0.0097), which is suitably close to zero to indicate partial miscibility and make plausible the fact that they will homogenize after a small amount of transreaction. The results shown in *Figure 6* are essentially the same as those proposed previously[10,11].

It is of interest to examine the effect of configuration on segmental interactions by analysing the behaviour of nylon-6I[4] in terms of the same ABC nomenclature as that detailed for MXD6. When using $\chi_{AB} = 8.534$, values of $\chi_{BC} = 8.02$ and $\chi_{AC} = -0.26$ are obtained. The former compares favourably with $\chi_{BC} = 8.0$, which was used to fit the data of MXD6. The negative value of χ_{AC}, when the aromatic polyamide of this structure is rationalized in this way, has been noted previously. A

Table 4 Interaction triads in blends of MXD6 and nylon-6I with aliphatic polyamides[a]

Pair interactions	Segment: Nylon-6I	Segment: MXD6
χ_{AAA}		
ABA	√	√
ABC	√	–
BCB	√	–
ACA	–	√
χ_{AAB}		
ABA	√	√
ABC	√	–
BCB	√	–
ACA	–	√
χ_{BAC}		
ABA	–	√
ACA	–	√
χ_{ABA}		
BCB	√	–
ACA	–	√
χ_{ABC}		
BCB	√	–

[a] √ indicates interaction is present

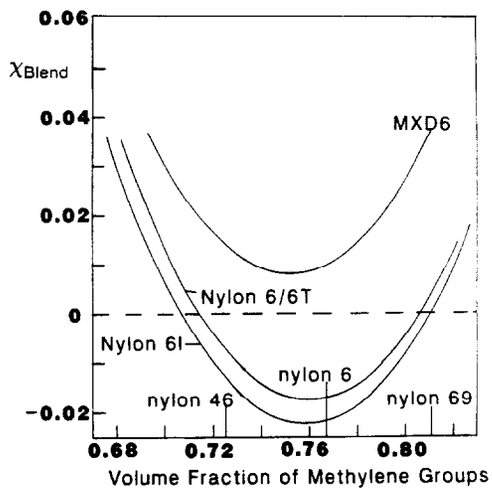

Figure 6 Calculated values of χ_{Blend} for blends of aliphatic polyamides with the polymers indicated

slightly positive (unfavourable) interaction between the methylene and phenyl groups, derived for blends of MXD6, is intuitively more easy to accept; however, at this stage it would be unwise to attach any physical significance to the source of this apparently favourable (attractive) interaction for the reasons outlined below. The differences between the χ_{ij}, parameters that result from the influence of nearest neighbours, may be accommodated by considering the localized effects of configuration. As noted earlier, χ_{Blend} is a free energy parameter, whereby each χ_{ij} parameter also has an entropic, χ_{ij}^{S}, and an enthalpic, χ_{ij}^{H}, compoent. The enthalpic component can be regarded as a hard core

Table 5 Values obtained for the segmental interaction parameters

χ_{ij}	Segment pair	Value
AB[a]	CH_2/NHCO	8.534
AC″[b]	CH_2/NHCO–  –CONH	1.693
AC′[b]	CH_2/NHCO–  –CONH	1.680
AC*[c]	CH_2/– 	0.100
AD[a]	CH_2/COO	2.233
BC″[b]	NHCO/NHCO–  –CONH	2.445
BC′[b]	NHCO/NHCO–  –CONH	2.432
BC*[c]	NHCO/– 	8.000
BD[a]	NHCO/COO	3.880
C*C″[c]	 /NHCO–  –CONH	1.680
C*D[c]	 /COO	1.500

[a] Values from ref. 17
[b] Values from ref. 4, scaled by the value of $\chi_{AB} = 8.534$
[c] Value estimated from ref. 22, scaled by the value of $\chi_{AD} = 2.233$

interaction which varies as $1/T$, while the entropic component may be influenced by the local environment, i.e. the configuration. A more formal treatment of the consequences of effects such as these are exemplified in the recent discussion of the influence of tacticity on polymer blend phase behaviour[23]. Therefore, an alternative approach to rationalizing the local entropic effects on the binary interaction model would be to examine the influence of configuration on Ψ, the segment volume fraction. From this perspective, a more appropriate parameter may be the 'effective' volume fraction, or a surface area fraction which would depend upon the local environment. There is obviously some difficulty in determining these quantities; however, it is believed that the differences observed, such as that noted for χ_{AC}, may be attributed to shortcomings of the nature described above.

A desirable outcome of treating polymer blend phase behaviour by using a binary interaction model based upon an elementary structural scheme is that interactions derived from one particular category of polymer blends will have an applicability, or at least some similarity, to those obtained from a different category of blends. It is possible to examine this feature by reference to aliphatic polyester/styrene–acrylonitrile copolymer blends. By applying a scaling factor, based upon $\chi_{AD} = 2.233$[17], a value of $\chi_{AC^*} \approx 0.16$ may be extrapolated from a study[22] involving blends of polymers containing the same chemical species but in considerably different environments. The latter value of χ_{AC^*} corresponds to methylene–phenyl interactions where the phenyl groups are those of polystyrene, and is a close approximation to the value $\chi_{AC^*} = 0.1$ shown in *Table 5*; similar procedures may be adopted to derive an estimate of $\chi_{C^*D} \sim 1.5$. These approximations also permit calculations of χ_{Blend} for MXD6 in copoly(ester–amides), specifically caprolactam/caprolactone copolymers. The results are shown in *Figure 7*, indicating that χ_{Blend} increases monotonically as the lactone content increases. Although a detailed experimental investigation has not been performed, a blend of MXD6 with a copolymer containing 16 mol% lactone exhibits complete phase separation with no evidence of the homogenizing effects

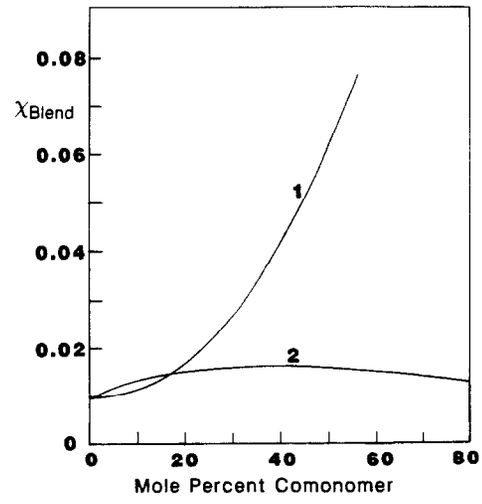

Figure 7 Calculated values of χ_{Blend} for blends of MXD6 with nylon-6 containing a comonomer: (1) caprolactone; (2) $-(CH_2)_6$ NHCO–*p*–Ph–CONH– (nylon-6T)

of transreaction even after heating for 5 min at 290°C. The copolymer also has a higher molar mass than that of nylon-6 which would also have the effect of reducing the level of miscibility. Nevertheless these observations suggest that χ_{Blend} for the latter (~ 0.0134) is greater than that of the MXD6/nylon 6 blend (~ 0.0097), which exhibits partial miscibility, and therefore provides qualitative support for the calculations presented.

Blends of MXD6 and aromatic polyamides. Nylon-6/6T can be classed as an ABC′ polymer (C′ = 1,4-phenyl substitution NHCO–Ph–CONH) and χ_{Blend} calculated, as shown in *Figure 6*, for blends containing various aliphatic polyamides. Presently there are no experimental observations from which to judge the accuracy of these calculations; however, it is of interest to note that the behaviour is projected to be similar to that of nylon-6I. Nylon-6/6T is a member of a series of polyamides which can be altered systematically by varying the content of caprolactam. The calculated trend for χ_{Blend} for these polymers in a blend with MXD6 is shown in *Figure 7*. An estimated value of $\chi_{C'C'} = 1.68$ was used to generate the curve shown.

The criteria applied in order to derive this quantity was that the value of χ_{Blend} for the blend MXD6/nylon-6/6T should be positive, to agree with the observed immiscibility noted in *Table 2*, but not so large as to preclude the occurrence of miscibility induced by a small amount of transreaction. It should be noted that there is very little margin for choice in the value of $\chi_{C'C'}$. Values outside the range 1.62–1.74 lead to unacceptable values of χ_{Blend}. Use of the information given above allows for estimating the behaviour of MXD6 (ABC*) in blends of aromatic polyamides. The results obtained for blends of poly (*n*-alkyl isophthalamides) are presented in *Figure 8*. These results signify that phase-separated blends will be formed exclusively, a result supported by the information given in *Table 2* for nylon-6I ($\chi_{Blend} \sim 0.0125$). The calculated value of χ_{Blend} may also be regarded as sufficiently close to zero to allow for the experimentally observed miscibility after thermally induced transreaction. Although exact calculations are possible to account for isomerism of the phenyl group its influence is only small, as noted earlier[3]. Accordingly, immiscibility should also be anticipated for blends of MXD6 with the additional aromatic polyamides, nylon-12IA, nylon-3Me6T and nylon-6I/T, results which can be confirmed experimentally, as shown in *Table 2*.

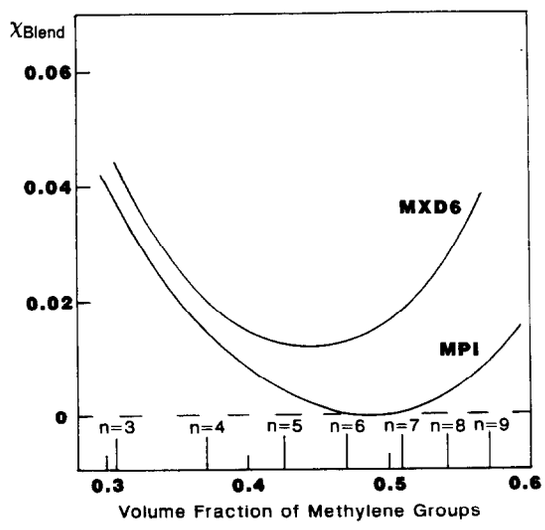

Figure 8 Calculated values of χ_{Blend} for blends of poly (*n*-alkyl isophthalamides) with MXD6 and MPI

It has been shown here that MXD6 and nylon-6I are both miscible with MPI. The latter contains only BCB and CBC triads and a tabulation of the various triad pairings with MXD6 and nylon-6I, similar to that given in *Table 4*, would again reveal the considerable microstructural disparity that exists between the two polymers; yet both are miscible with MPI. A simple analysis of MPI/nylon-*n*I blends, as ABC copolymers, reveals that a large window of miscibility should be expected[21]. Alternatively, if MPI is defined as a C*C″ copolymer (C″ symbolizes 1,3-phenyl substitution) and the nylon *n*I materials as AC″ copolymers, then the use of the χ_{ij} parameters noted in *Table 5* forces the window of miscibility to disappear completely. Obviously the $\chi_{C'C''}$ parameter derived from MXD6 in the nylon *n*I polymers is far from suitable for describing the configuration of C in MPI. At the moment there is insufficient information to resolve the most appropriate way of representing MPI. An empirical solution may be obtained by defining critical limits ($y = 0.48$ and 0.49, as points where $\chi_{Blend} = 0$ for MPI in nylon *n*I polymers, where y = volume fraction of methylene groups in nylon *n*I) for miscibility based upon the experimental observations[21] and by using $\chi_{AB} = 8.534$. The calculations, shown in *Figure 8*, provide values of $\chi_{BC} \approx 11.0$ and $\chi_{AC} \approx 0.16$ and describe a reasonable fit to the experimentally observed behaviour. Once again a small but unfavourable methylene–phenyl interaction is obtained. However, the amide–phenyl interaction is considerably larger than that (≈ 8.00) noted earlier. This result would also provide a strong driving force (net repulsive interaction) for miscibility between MPI and other polymers such as the aliphatic polyamides. There have been some reports[24,25] in the literature to support such behaviour; however, the most immediate result of interest is that calculations made for a blend of MXD6 (ABC*) and MPI (BC″) indicate the formation of a miscible mixture ($\chi_{Blend} \approx 0.03$), a result which is in agreement with the experimentally observed behaviour reported here. It is unlikely that all of the quantitative aspects of the discussion presented above are correct. Nevertheless, there is a qualitative consistency to much of the behaviour described which can be rationalized by a simple model.

CONCLUSIONS

The application of a binary interaction model to describe the phase behaviour of polyamide blends has been extended to include polymers which contain identical chemical species in exactly the same proportions but arranged in a different configuration. In order to do so, it has been necessary to consider the local environment of the species or segments in terms of their respective triad groupings. By comparing the behaviour of nylon-6I and MXD6 in aliphatic polyamides the parameters derived from the model have been shown quite often to be only slightly affected by these sequence effects. However, slight differences have also been shown to have a profound effect on the mixing behaviour for certain blends. In addition to the above, calculations have been

presented to describe the phase behaviour of MXD6 in aromatic polyamides and copoly(ester–amides) derived from caprolactam/caprolactone copolymers. This kind of linkage will eventually allow for qualitative estimations concerning the blending behaviour of aromatic polyesters. This will form the subject of a future communication.

Some of the information presented has required the empirical conformity of data points to the model in order to derive the predictions shown. Accordingly, the quantitative accuracy of the projected behaviour must be regarded only as tentative until there is additional experimental information available for further input. Nevertheless, the results provide a valuable insight into the effects of configuration upon the mixing behaviour of polyamides. An important feature of the discussion presented here is that a quantitative explanation is provided for the observed immiscibility of the blend MXD6 and nylon-6I. Clearly, any solubility parameter arguments indicate that this blend should be miscible. Similarly, any argument based upon the reasoning that the miscibility between the aromatic and aliphatic polyamides arises from a favourable hydrogen-bonding interaction between the respective aliphatic and aromatic amide groups to overcome the dispersive interaction is also compromised by the latter observation. A further notable feature of the discussion above is that some values of the segmental interaction parameters (AC^* and C^*D), extracted from independent studies involving polymers with considerably different backbones, have found a suitable application to polymers containing the same chemical species. Small differences have been noted, but unfortunately there is no quantitative framework available from which to rationalize these differences.

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