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Influence of Structure on Phase Behavior of Polyamide Blends

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ABSTRACT: An examination of phase phenomena of blends of several aromatic polyamides in a comprehensive series of aliphatic polyamides and copolyamides has been performed. In particular, the predictive ability of a binary interaction model to correlate experimental observations with fundamental chemical constitution has been addressed. The aromatic polyamides concerned contain a variety of complex chemical functionalities, which differ considerably from those upon which the model was founded. Nevertheless, it has been found that the model still provides a good description of experimental behavior. By incorporating these new observations into the model, additional boundary conditions have been estimated to provide semiquantitative corrections such that agreement between theory and experiment is improved.

Introduction

A recent series of papers[1-5] has made considerable progress toward defining the structural and chemical features that influence phase behavior of aliphatic and aromatic polyamide blends. Experimental observations have revealed the existence of simple relationships between structure and miscibility that are complimented by theory based upon a binary interaction model. This type of approach, established on the now widely applied copolymer repulsion effect,[6-8] has found great utility in a variety of blend systems.[9-14] Briefly, the model entails equating an effective interaction parameter, χ_{blend}, with terms representing the summation of intra- and intermolecular segmental exchange interactions. The choice of segments has often been based upon monomer species present in the polymer chains; however, some accounts have rationalized behavior in terms of elementary chemical functionalities, e.g., ester, methylene, etc. This definition may be considered the most desirable since parameters determined by using a fundamental nomenclature may have a wider applicability to other blend systems. However, this also presents the most difficulty when trying to obtain meaningful data.

As part of a continuing effort to fully develop and explore the potential of a group contribution approach to characterize phase phenomena in this genus of polymer blends, this paper addresses the influence of structure on phase behavior of aromatic polyamides in blends of aliphatic polyamides. Moreover, the timely addition of this information to the literature lends further support to the arguments developed in earlier contributions. This is of particular interest considering recent studies on polyamide blends by other workers,[15,16] which although providing data consistent with existing theory, is being interpreted in a completely different framework involving hydrogen bonding. Although it is still open to question whether or not such an approach is capable of accommodating all observations reported thus far, these approaches are useful in allowing the true nature of phase-determining interactions in polyamide blends to be determined.

Theoretical Background

The early contributions[1-4] on this subject in polyamide blends based much of the analysis upon the general notion that aromatic polyamides could be considered to represent copolymers composed appropriately of methylene, amide, and phenyl mers, denoted as A–C, respectively. Although this remains essentially a valid definition, certain qualifying conditions must be introduced. A more recent discussion[5] of this subject recognizes that while such a broad generalization was useful for exploratory purposes, the configuration of the various mers would probably exercise a significant influence. It was proposed that this would be particularly true for the aromatic polyamides. Subsequent experimental observations,[17,18] involving polyamide blends with a constituent possessing a structural variation of the nature described, have confirmed these suspicions. These results do not invalidate the general approach but simply reflect the importance of recognizing χ_{blend} as a free-energy parameter. Composed of enthalpic and entropic contributions, which will almost certainly be influenced by structure, this interpretation was highlighted most recently by ten Brinke.[19]

In view of the configurational restrictions mentioned above, aromatic polyamides of the generic structure $-(CH_2)_nNHCOPhCONH-$ can be regarded as random copolymers with two differing nomenclatures.[5] One of these is the simple $A_yB_zC_{1-y-z}$ classification and the other is $A_yC'_{1-y}$ where C′ represents the 1,4-amide-substituted (T) phenyl mer. The subscripts x, y, etc., refer to the respective mer contribution to the molar volume of the polymer. Similarly, the use of a C″ notation, which refers to 1,3-substitution (I), introduces the potential to address structural isomerism of the phenyl mer, a feature that although always recognized as having a possible influence, was usually discarded in the past. For the purposes of this discussion, the classification of aliphatic polyamides and copolyamides as random copolymers of A and B functionalities is still considered appropriate.

Explicit details of the model applied in this study may be found elsewhere;[1-5] however, a brief summary will be provided here to ensure continuity. On the basis of the simple nomenclature, it can be shown that for a mixture of an aliphatic polyamide (A_xB_{1-x}) and an aromatic polyamide ($A_yB_zC_{1-y-z}$) an expression for χ_{blend}, the effective interaction parameter, is given as eq 1. As a first-order

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

approximation, of $\chi_{\text{blend}} < 0$, then miscibility will be favored. The converse should be expected if $\chi_{\text{blend}} > 0$.

Experimental evidence, from studying the phase behavior of blends containing copolyamides,[4] has shown that values of the segmental interaction parameters can be written as $\chi_{AB} = 7.984$, $\chi_{BC} = 7.460$, and $\chi_{AC} = -0.288$.

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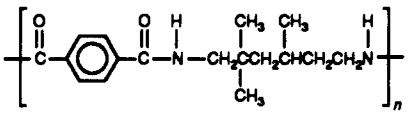
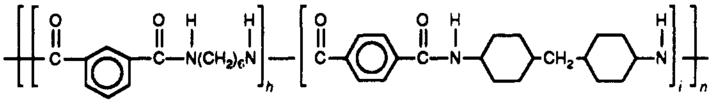
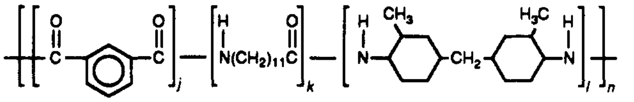
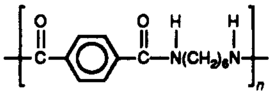
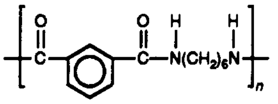
Table I
Structure and Properties of the Aliphatic Polyamides

polyamide	volume fraction of methylene units (x)	T_g,[a] °C	T_m,[a] °C	$M_n \times 10^{-3}$	$M_w \times 10^{-3}$
nylon 46 (Stanyl; Allied Chemical)	0.7255	58	291	22	100
2P/CL copolyamide[b] 24.1/75.9	0.749	48	183	13	24
2P/CL copolyamide[b] 17.6/82.4	0.754	44	168	17	40
2P/CL copolyamide[b] 12.5/87.5	0.758	44	201	29	77
2P/CL copolyamide[b] 6.5/93.5	0.763	43	215	38	118
nylon 66 (Zytel 101; Du Pont)	0.7676	45	262	31	92
nylon 6 (Zytel 211; Du Pont)	0.7676	41	223	41	120
CL/LL copolyamide 79.9/20.1[b]	0.804	36	196	81	163
CL/LL copolyamide 74.7/25.3[b]	0.811	32	187	84	179
nylon 69 (Aldrich Chemical Co.)	0.8111	28	210	15	80
nylon 610 (Aldrich Chemical Co.)	0.8222	25	222	12.5	87.5
CL/LL copolyamide[b] 59.3/40.7	0.831	27	NO[c]	310	1400
CL/LL copolyamide[b] 55.6/44.4	0.835	31	NO[c]	282	750
CL/LL copolyamide[b] 51.2/48.8	0.840	33	NO[c]	244	770
nylon 612 (Zytel 151; Du Pont)	0.8409	40	219	15	65.5
CL/LL copolyamide[b] 43.8/56.2	0.847	26	124	290	950
CL/LL copolyamide[b] 36.0/64.0	0.854	28	132	210	820
CL/LL copolyamide[b] 27.7/72.3	0.861	27	137	190	530
CL/LL copolyamide[b] 19.5/80.5	0.867	26	147	240	590
nylon 11 (Rilsan BMNO; Rilsan Corp.)	0.8685	29	189	25	65
CL/LL copolyamide 11.9/88.1	0.872	26	157	130	680
nylon 12 (Rilsan AESNO; Rilsan Corp.)	0.8790	35	180	16	57

[a] Determined by DSC on samples quench cooled from the melt. [b] Copolymers synthesized as described previously.[4] [c] NO = not observed.

Table II
Structure and Properties of the Aromatic Polyamides

			T_g, °C	$M_n \times 10^{-3}$	$M_w \times 10^{-3}$
nylon 3Me6T[b]			147	20	63
nylon 6IcoTA[a,c]			156	18	45
nylon 12IA[a,d]			154	29.5	62.5
nylon 6IcoT[c]		(Zytel 330)	127	14	50
		(Selar 3426)	123	12	47
nylon 6I[d]			118	15	22

[a] h/i is approximately 0.69/0.31 in a random copolymer. $j/k/l$ is approximately 1/1.06/1 in a random copolymer. [b] 100% 1,4-phenyl substitution. [c] 1,3-/1,4-phenyl substitution is approximately 2/1. [d] 100% 1,3-phenyl substitution.

However, as described previously, it is not possible at this stage to separate amide and phenyl groups in the configuration given here. Therefore, if entropic contributions are again neglected and the simple nomenclature is replaced by defining aromatic polyamides as $A_yC'_{1-y}$ copolymers, then the expression for χ_{blend} is given by eq 2. Under these circumstances, $\chi_{BC'} = 2.275$ and $\chi_{AC'} =$

$$\chi_{\text{blend}} = (y - x)(1 - x)\chi_{AB} + (1 - y)(1 - x)\chi_{BC'} + (x - y)(1 - y)\chi_{AC'} \quad (2)$$

1.5713. It should be emphasized that the quantitative behavior of the blends is the same irrespective of the equation and respective χ_{ij} employed, provided that the aromatic polyamide being considered is always in the configuration described previously.

Experimental Section

Materials. A summary of the structure and properties of the aliphatic polyamides and copolyamides used in this study is presented in Table I. The synthesis and characterization of the 2-pyrrolidinone/caprolactam (2P/CL) and caprolactam/laurolactam (CL/LL) copolyamides has been described previously.[4] The structure and properties of the aromatic polyamides are presented in Table II. Nylon 6IcoTA (Du Pont) is an amorphous polyamide containing a mixture of 1,3- and 1,4-benzenedicarboxylic acids in a molar ratio of approximately 2/1. These acids are polymerized with a stoichiometric mixture of 1,6-hexanediamine and bis(4-aminocyclohexyl)methane in a molar ratio indicated as 0.69/0.31 (see Table II). Nylon 6IcoT (Zytel 330 and Selar 3426; Du Pont) have been documented as equivalent copolymers as shown in Table II. This is not completely correct since Zytel 330 also contains approximately 1 mol % of the same alicyclic diamine as that contained in nylon 6IcoTA. Nylon 6I (Nydur T40; Bayer) is the product of condensation of pure iso-

Table III
Calculated Values of Segmental Interaction Parameters

χ_{ij}	mer structure	value
χ_{AB}	CH_2/NHCO	7.984[a]
χ_{BC}	NHCO/Ph	7.460[a]
χ_{AC}	CH_2/Ph	−0.288[a]
$\chi_{BC'}$	NHCO/NHCO-1,4-Ph-CONH	2.275[a]
$\chi_{AC'}$	CH_2/NHCO-1,4-Ph-CONH	1.571[a]
$\chi_{BC''}$	NHCO/NHCO-1,3-Ph-CONH	2.288
$\chi_{AC''}$	CH_2/NHCO-1,3-Ph-CONH	1.584
$\chi_{A'B}$	cyclohexane/NHCO	7.984
$\chi_{A'C''}$	cyclohexane/NHCO-1,3-Ph-CONH	1.553
$\chi_{A'C'}$	cyclohexane/NHCO-1,4-Ph-CONH	–

[a] See refs 4 and 5.

phthalic acid with 1,6-hexanediamine.

The structure of nylon 12IA (Grilamid TR55; Emser Industries), also shown in Table II, is represented as a random copolymer of isophthalic acid (P), 12-aminododecanoic acid (L), and bis(4-amino-3-methylcyclohexyl)methane (B). NMR analysis has indicated the molar ratio of these constituents is 1.0: 1.057:1.0, and a diad analysis has shown the relative proportion of the various linkages to be LL = 12%, PL = 23%, PB = 43%, and LB = 23%.

Procedures. Blends were prepared by coprecipitation from a common solvent of trifluoroethanol/methylene chloride (3/2, v/v) into diethyl ether in a manner similar to that described in previous studies.[1-5] All blends were dried extensively in vacuo at ambient conditions and then subjected to further drying at approximately 80 °C.

Thermal analysis was performed by using a Perkin-Elmer series VII differential scanning calorimeter at a program heating rate of 10 °C/min. The glass transition temperature, T_g, was recorded as the onset, and the melting point, T_m, was noted as the maximum of the melting endotherm. Conclusions with regard to phase phenomena are again based upon observations of the T_g behavior of the blends. A single glass transition temperature, usually below that of linear additivity, has been assumed to indicate miscibility. Additional information based on qualitative observations of crystallization kinetics, enthalpy recovery measurements,[20] and the incremental change of heat capacity at T_g has also been used. Unless stated otherwise, analysis was restricted to 50/50 w/w blend mixtures. It is therefore implicit that this composition represents the minimum of any existent cloud-point curve.

Molecular weight analysis was effected by size-exclusion chromatography (GPC) at 110 °C using *m*-cresol as the solvent and 0.02 M lithium bromide as an antioxidant. Calibration was provided with polystyrene standards, and therefore the values reported are relative to this standard. The structural characterization of the aromatic polyamides was performed by proton NMR at 60 °C using hexafluoroacetone as solvent.

Results and Discussion

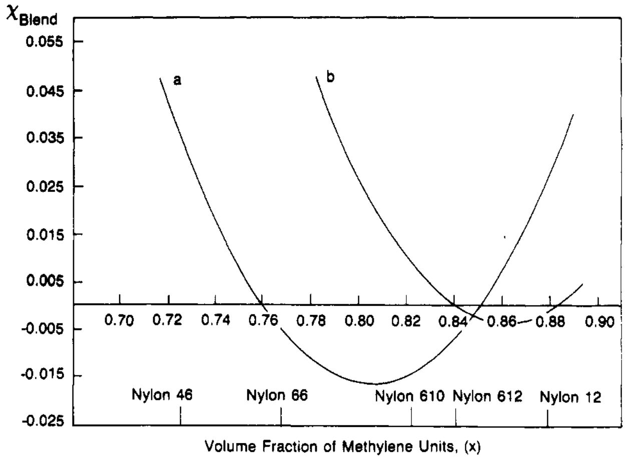


Figure 1. Calculated values of χ_{blend} of nylon 3Me6T (a) and nylon 12IA (b) in aliphatic polyamides.

Table IV
Summary of the Thermal Properties and Phase Behavior of Nylon 12IA/Aliphatic Polyamide Blends

blend component[a]	volume fraction of methylene units (x)	T_g,[b] °C	experimentally obsd phase behavior
nylon 6 (41)	0.7676	42 152	I
nylon 610 (25)	0.8222	32 148	I
CL/LL 59.3/40.7 (27)	0.831	38 147	I
CL/LL 55.6/44.4 (31)	0.835	38 145	I
CL/LL 51.2/48.8 (33)	0.840	44 139	I
nylon 612 (40)	0.8409	45 140	PM
CL/LL 43.8/56.2 (26)	0.847	46 131	PM
CL/LL 36.0/64.0 (28)	0.854	64	M
CL/LL 27.7/72.3 (27)	0.861	62	M
CL/LL 19.5/80.5 (26)	0.867	60	M
nylon 11 (29)	0.8685	43 123	PM
CL/LL 11.9/88.1 (20)	0.872	43 na	PM
nylon 12 (35)	0.879	36 150	I

[a] Number in parentheses is the pure component T_g. I = immiscible. PM = partially miscible. M = Miscible. [b] T_g of pure nylon 12IA is approximately 154 °C. na = not available.

Phase Behavior of Nylon 12IA in Aliphatic Polyamides and Copolyamides. The chemical structure shown in Table II for nylon 12IA represents a considerable departure from nylon 3Me6T, the polymer upon which the model parameters were founded. Nevertheless, by assuming that the alicyclic moieties represent an ensemble of methylene units, it is possible to assign this polymer to a class of $A_yB_zC_{1-y-z}$ copolymers, resulting in values of y = 0.7514, z = 0.1376, and $1 - y - z$ = 0.1110. These quantities have been obtained by using the known values for group contributions to the molar volume of polymers.[21] For example, in this context, a disubstituted alicyclic unit has been rationalized as a hydrocarbon unit of four methylene ($-CH_2-$) and two >CH– groups. Incorporating this information into eq 1 and using the appropriate segmental interaction parameters determined from the behavior of blends containing nylon 3Me6T, given in Table III, results in the calculated curve b shown in Figure 1. The curve a established for nylon 3Me6T is also shown for comparison and illustrates the substantial difference in calculated blend behavior between these two polymers. Before proceeding further, it should be emphasized that although the calculated behavior for nylon 12IA can be improved upon, the experimentally observed behavior closely imitates this projection even without the inclusion of the refined description that will be provided in later sections. This situation is repeated for blends containing nylon 6IcoT and nylon 6IcoTA, as will also be described subsequently.

A summary of the experimentally observed phase behavior of nylon 12IA in selected polyamides and copolyamides is shown in Table IV. The data indicate a region of miscibility between values of x of approximately 0.85 and 0.87, respectively. This is a slightly narrower range than that given by calculations (approximately 0.84–0.88) as shown in Figure 1. Thermograms illustrating some of the more relevant data provided in Table IV are shown in Figures 2 and 3, respectively. Thermograms A and B in Figure 2 are for a blend containing nylon 11. The quench-cooled blend (B) displays a T_g at 43 °C (cf. nylon 11; T_g = 29 °C) and a slight crystallization exotherm, a feature normally absent in pure nylon 11. This exotherm conceals a T_g for the nylon 12IA rich phase, which becomes evident in the crystallized blend (thermogram A). Enthalpy recovery measurements[3,20] also support the conclusion of partial miscibility, with a recovery peak for the blend occurring at a higher temperature than that of pure

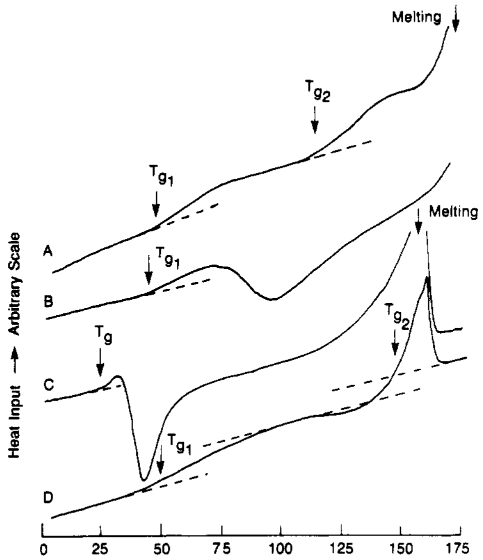


Figure 2. Representative thermograms of blends containing nylon 12IA: (A) nylon 11 ($x = 0.8685$, crystallized), (B) nylon 11 ($x = 0.8685$), (C) CL/LL copolyamide ($x = 0.872$, pure polymer), (D) CL/LL copolyamide ($x = 0.872$).

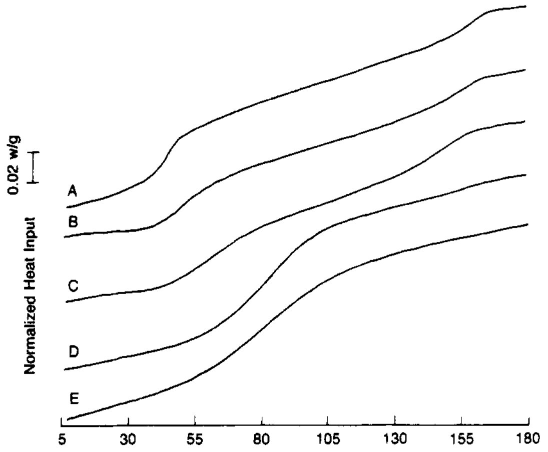


Figure 3. Representative thermograms of blends containing nylon 12IA: (A) CL/LL copolyamide ($x = 0.831$), (B) CL/LL copolyamide ($x = 0.840$), (C) CL/LL copolyamide ($x = 0.847$), (D) CL/LL copolyamide ($x = 0.861$), (E) CL/LL copolyamide ($x = 0.867$).

nylon 11. Interpretation of phase behavior in crystallized blends can be made difficult if segregation of species occurs during the crystallization process. This can result in the appearance of a phase-separated blend, which when prepared in the purely amorphous state may be completely miscible.[22] This phenomenon, however, is believed not to be a factor for the blend containing nylon 11. Partial miscibility of nylon 12IA in a CL/LL copolyamide ($x = 0.872$) is also clearly evident as noted in thermograms C and D in Figure 2. From these observations and the fact that nylon 11 is partially miscible, the upper bound for miscibility has been estimated to be $x = 0.8685$, the value of x for nylon 11.

For the lower bound, the thermograms A–C shown in Figure 3 illustrate the gradual crossover to miscibility as x increases, signifying a critical limit for miscibility estimated to be at $x = 0.847$; the partial miscibility observed in this blend (thermogram C) has been attributed entirely to entropic effects. The thermograms D and E in Figure 3, for blends where $x = 0.861$ and 0.867, respectively, are indicative of miscibility. However, the thermogram E has a very broad transition, which supports a belief that this blend is only just miscible. It is also worth noting that, for blends marginally outside this critical limit, the relatively large shift of the T_g's of the phases from their respective pure components suggests that they were only just immiscible. This is a subjective observation; however, it supports the projection of a shallow miscibility curve as shown by b in Figure 1. No critical behavior in the form of a lower critical solution temperature, LCST, was observed for any of the blends. In summary, the experimentally observed critical limits are condensed to a region within those currently projected by calculation; however, the minimum of the miscibility curve appears to be close to the calculated value of approximately $x = 0.86$. A quantitative account to accommodate these observations will be provided in a latter section.

Table V
Summary of the Thermal Properties and Phase Behavior of Nylon 6IcoTA/Aliphatic Polyamide Blends

blend component[a]	volume fraction of methylene units (x)	T_g,[b] °C	experimentally obsd phase behavior
nylon 46 (58)	0.7255	64 154	I
2P/CL 17.6/82.4 (44)	0.754	53 128	PM
2P/CL 12.5/87.5 (44)	0.758	63 na	PM
2P/CL 6.5/93.5 (43)	0.763	72	M
nylon 66 (45)	0.7676	77	M
nylon 69 (28)	0.8111	72	M
nylon 610 (25)	0.8222	55 147	PM
CL/LL 59.3/40.7 (27)	0.831	41 155	I
nylon 612 (40)	0.8409	30 158	I

[a] Number in parentheses is the pure component T_g. I = immiscible. M = miscible. PM = partially miscible. [b] T_g of pure nylon 6IcoTA is approximately 156 °C. na = not available.

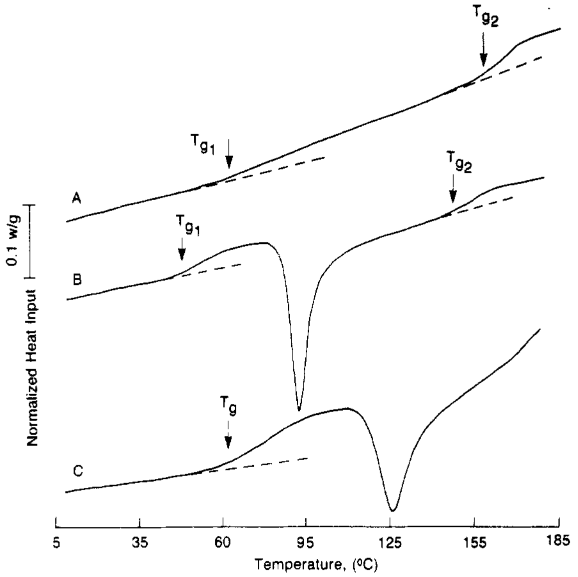


Figure 4. Representative thermograms of blends containing nylon 6IcoTA: (A) nylon 46, (B) nylon 610, (C) nylon 69.

Phase Behavior of Nylon 6IcoTA in Aliphatic Polyamides and Copolyamides. A previous paper[2] has already documented the behavior of nylon 6IcoTA in blends containing nylon 12 and nylon 66, respectively. A more comprehensive and systematic study of blends containing aliphatic polyamides has now been conducted, the results of which are summarized in Table V. Some of the thermograms supporting these conclusions are provided in Figures 4 and 5. Thermogram A in Figure 4 typifies phase separation in a blend of nylon 6IcoTA and nylon 46. The blend containing nylon 610 (thermogram B) also shows two distinct T_g's, which contrast with the single T_g obtained

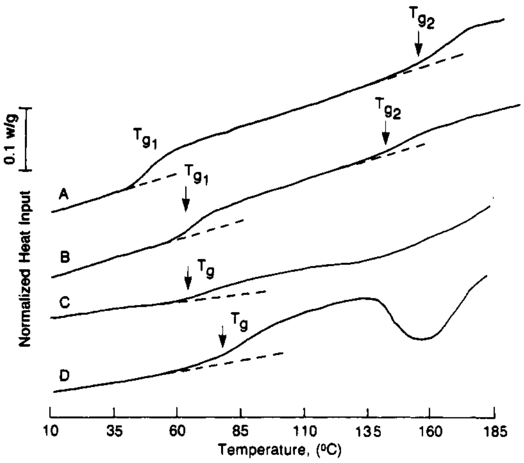


Figure 5. Representative thermograms of blends containing nylon 6IcoTA: (A) CL/LL copolyamide (x = 0.831, not to scale), (B) 2P/CL copolyamide (x = 0.754), (C) 2P/CL copolyamide (x = 0.758), (D) 2P/CL copolyamide (x = 0.763).

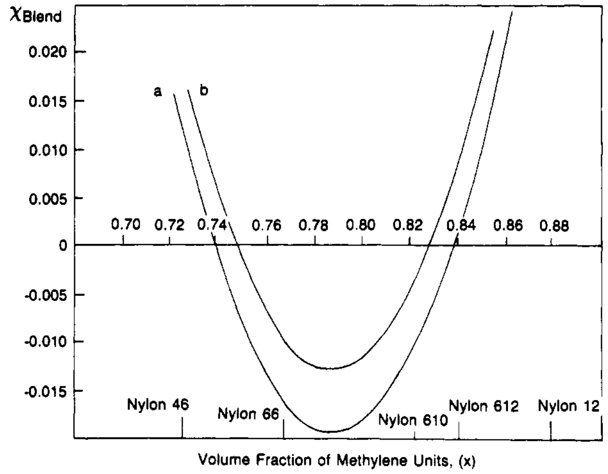


Figure 6. Calculated values of χ_{blend} of nylon 6IcoTA in aliphatic polyamides: (a) as an ABC copolymer, (b) as an $A_yA'_yC''_{1-y-y'}$ copolymer.

in a blend of nylon 69 (thermogram C) which indicates miscibility. In addition to this, the incremental change of heat capacity at T_g in the latter blend is almost twice that of the individual values shown for the blend containing nylon 610, which was shown to be immiscible. The thermogram A in Figure 5 illustrates the immiscibility of a blend where x = 0.831, which, although not drawn to the same scale, emphasizes more clearly phase separation.

Inspection of thermograms provided in Figure 5 demonstrates the continued miscibility (thermogram D) of nylon 6IcoTA in copolyamides with values of x below that of nylon 66 (x = 0.7676). However, the lower bound for miscibility must be reasonably close to x = 0.76 since the blend with x = 0.758 illustrates only partial miscibility (thermogram C). The latter blend possesses a rather broad T_g with an onset (T_g = 53 °C) substantially below that anticipated for a completely miscible system. Decreasing x further to 0.754 (thermogram B) yields more complete phase separation.

The experimental observations, noted above, when compared to calculated behavior as shown by curve a in Figure 6, again reveal approximate agreement with theory. In this comparison, the nylon 6IcoTA has been rationalized as a simple ABC copolymer as described by eq 1. However, again there is an important noticeable discrepancy, which is manifest as a narrowing of the miscibility gap as determined by experiment. The data in Table V indicate critical limits of x at approximately 0.75 and 0.82, respectively, compared to 0.74 and 0.84 as shown in Figure 6. This still represents a remarkable level of agreement between the observations and simple theory, particularly in view of the chemical dissimilarity of nylon 3Me6T when compared to nylon 6IcoTA.

Phase Behavior of Nylon 6IcoT and Nylon 6I in Aliphatic Polyamides and Copolyamides. This section directs attention to the influence of structural isomerism of the phenyl group in the aromatic polyamide. Although a detailed description, both theoretical and experimental, of the behavior of nylon 6IcoT has already been presented,[2,4] there is presently no information describing the behavior of nylon 6I.

Nylon 6I contains only the 1,3-substituted phenyl derivative (see Table II), and, although the model, as it exists presently, is unable to distinguish between this material and nylon 6IcoT or poly(hexamethyleneterephthalamide) (nylon 6T), subtle differences of behavior attributable to this minor structural feature have been detected. As mentioned in the Experimental Section, there is a slight compositional difference between the two sources of nylon 6IcoTA investigated (Zytel 330 and Selar 3426). Presently, no detectable differences have been found between these slightly different nylon 6IcoT polymers when blended with semicrystalline nylons (see Table VI). This is a reasonable expectation owing to the relatively small amount of the alicyclic component in the former polymer.

All three of these very similar aromatic polyamides were found to be immiscible with nylon 610 as documented in Table VI. Calorimetric evidence illustrating multiple T_g behavior is also provided in Figure 7. Similarly, both forms of nylon 6IcoT were determined to be completely miscible with nylon 69 as can be seen by inspection of Figure 8 (thermograms C and D) and the data contained in Table VI. However, nylon 6I was found to be at best only partially miscible in nylon 69 as can also be seen in Figure 8 (thermogram B). A rather low blend T_g of 43 °C, in addition to an incremental change of heat capacity at T_g, of approximately half that of the miscible blend of nylon 6IcoT/nylon 69 provides strong evidence against miscibility. Figure 8 also displays a thermogram (A, not to the same scale) of the crystallized blend showing the presence of two T_g's, which provides further evidence of a multiphase system. The behavior of blends of nylon 6I and nylon 6IcoT with aliphatic copolyamides x = 0.804 and 0.811, respectively, also provide continuity to these arguments concerning phase behavior as shown in Table VI. The seemingly aberrant blend in Table VI (x = 0.811, containing nylon 6IcoT) indicating only partial miscibility is, in fact, extremely close to complete miscibility. The blend transitions were found to be almost completely merged, and it is believed that the principal cause of this is the high molar mass of the copolyamide compared to that of nylon 69. The blend of nylon 69 containing nylon 6IcoT was found to be completely miscible.

Although the structural differences of these polymers may be considered only minor, the blends described above involve aliphatic polyamides whose methylene content (x = 0.8111 for nylon 69 and x = 0.8222 for nylon 610) places the blends close to the upper critical limit for miscibility ($x \simeq 0.814$).[4] Consequently, different behavior may be anticipated. Conversely, nylon 46 is a semicrystalline nylon whose methylene content (x = 0.7255) is well within the calculated lower critical limit ($x \simeq 0.685$) for miscibility[4] for these blends. Accordingly, a blend of the latter with nylon 6I was found to be miscible (see Table VI) as

Table VI
Summary of the Thermal Properties and Phase Behavior of Blends[a] of Nylon 6IcoT and Nylon 6I in Selected Aliphatic Polyamides (Numbers in Parentheses Are Measured Values of T_g)

	volume fraction of methylene units (x)	nylon 6IcoT (Zytel 330)	nylon 6IcoT (Selar 3426)	nylon 6I
nylon 46 (58)	0.7255	M (77)		M (78)
nylon 66 (45)	0.7676	M (72)		M (70)
CL/LL 79.9/20.1 (36)	0.804		M (61)	M (67)
CL/LL 74.7/25.3 (32)	0.811		PM (56, 87)	PM (44, 95)
nylon 69 (28)	0.8111	M (65)	M (66)	PM (43, 111)
nylon 610 (25)	0.8222	I (35, 127)	I (31, 118)	I (30, 116)

[a] 50:50 wt %. I = immiscible. M = miscible. PM = partially miscible.

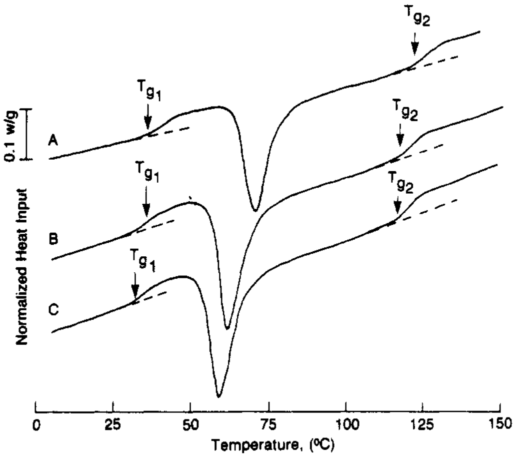


Figure 7. Representative thermograms of blends containing nylon 610; (A) nylon 6IcoT (Zytel 330), (B) nylon 6IcoT (Selar 3426), (C) nylon 6I.

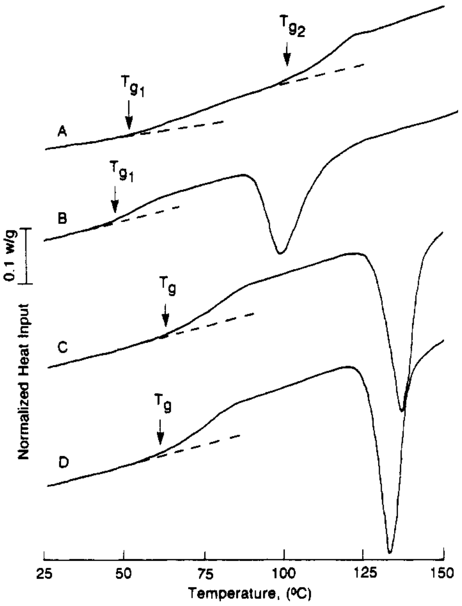


Figure 8. Representative thermograms of blends containing nylon 69: (A) nylon 6I (crystallized, not to scale), (B) nylon 6I, (C) nylon 6IcoT (Zytel 330), (d) nylon 6IcoT (Selar 3426).

expected. These calculations are, of course, based upon the behavior of the 1,4-substituted isomer. However, the miscibility of nylon 6I in a blend of nylon 66 suggests that the only currently observable effect of this compositional variable occurs in blends close to the critical limits for miscibility.

Theoretical Considerations

Influence of the Phenyl Component. The data presented in the previous sections again provide ample evidence to illustrate the effectiveness of a simple binary interaction model to account for phase behavior in mixtures of aromatic/aliphatic polyamides. It should be remembered that the original analysis was based upon the behavior of nylon 3Me6T (see Table II) in blends of the latter, and, accordingly, all of the predictive calculations are directed strictly to blends of aromatic polyamides containing only the 1,4-substituted phenyl isomer. Although it is known that isomerism of this type can influence segmental interactions, the close similarity of experimental behavior with theory for nylon 6IcoT, which contains predominantly the 1,3-substituted isomer, suggests that its influence in polyamide blends is probably small. However, there is alternative behavior to suggest that this may not be totally correct. In the following sections, an approximation to include this structural feature will be advanced to improve the agreement between theory and experiment. In doing so, it is necessary to adjust the nomenclature to that introduced previously and which is satisfied by eq 2. It should also be emphasized that these complicating adjustments have been made because they establish a foundation for explaining the subtle differences observed.

With this nomenclature nylon 6I is an $A_yC''_{1-y}$ copolymer, where C'' represents the 1,3-substituted phenyl isomer. In blends of A_xB_{1-x} aliphatic polyamides with the latter, χ_{blend} is given in form by eq 2. Since χ_{AB} is known, only two simultaneous equations are necesary to solve for $\chi_{AC''}$ and $\chi_{BC''}$. These can be formulated by using the experimental behavior described previously. The fact that nylon 6I is partially miscible in nylon 69 ($x = 0.8111$) and the information in Table VI allow an estimation of the upper bound for miscibility to be $x = 0.81$. This value contrasts with that calculated for the pure 1,4-isomer of $x = 0.8142$. Since nylon 12IA also contains only the 1,3-substituted phenyl isomer, the second equation could, in principle, be formulated from an experimentally observed critical limit for this polymer. However, the behavior of this material, almost certainly contains a contaminating contribution from the alicyclic component, and therefore it should not be incorporated into the required calculations. Consequently, an assumption will be made. Continuing within the spirit of a mean-field approximation, it will be assumed that the change in limiting condition is symmetrical about the x axis. Thus the lower bound is shifted to a higher value by an equal amount from $x = 0.7027$, for the pure 1,4-isomer, to $x = 0.7069$, for the pure 1,3-isomer.

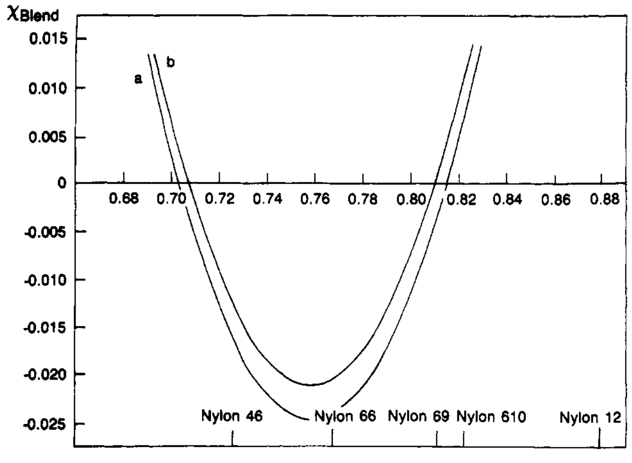


Figure 9. Calculated values of χ_{blend} of aromatic polyamides, $-NHCOPhCONH(CH_2)_6-$, in aliphatic polyamides: (a) $A_yC'_{1-y}$ (Ph = 1,4-phenyl isomer), (b) $A_yC''_{1-y}$ (Ph = 1,3-phenyl isomer).

There is some evidence[15] to suggest that 1,3-phenyl substitution may have a greater influence in determining the value of the lower bound than that of the upper bound. The estimation of these critical limits provides boundary conditions to solve for $\chi_{BC''}$ and $\chi_{AC''}$; the values obtained are listed in Table III. The estimation of the lower bound is somewhat speculative; however, doing so enables a number of calculations to be performed that otherwise would not be possible. The close agreement between the experimental observations and the calculations has been considered sufficient justification for the approximations applied.

The previous discussion is summarized schematically in Figure 9, where the projection (curve a) represents a calculation for nylon 6T. The calculated miscibility curve for nylon 6I (curve b) is in agreement with the experimental data shown in Table VI. The behavior of nylon 6IcoT, which contains a mixture of the two isomers but has the same chemical compositions as the nylon 6I, resides between these two extremes but is still consistent with experimental observations. It should be noted that since nylon 6IcoT contains a mixture of 1,3- and 1,4-isomers, an additional term involving a $\chi_{C'C''}$ interaction is present in the equation for χ_{blend}. Since $\chi_{C'C''}$ is expected to be positive, this would result in slightly lower values of χ_{blend}. However, this extra term is also expected to be very small, and since it is not possible at this stage to obtain an estimation, it is a reasonable assumption to assign a zero value.

Care should be exercised when assumptions such as that described above are introduced. It is an obvious temptation to assign a zero value to interactions such as a $\chi_{C'C''}$ interaction because of their extremely close chemical similarity. However, previous work[23] has demonstrated that for some polymers this will not always be true. A large segmental interaction parameter ($\chi = 0.1$) between *o*- and *p*-chlorostyrene units has been deduced as a principal driving force for miscibility in blends of these copolymers with a homopolymer. The fact that nylon 6IcoT behaves closely to the pure nylon 6I suggests that a similar situation does not occur for aromatic polyamides.

Influence of the Alicyclic Component. The information presented in the previous section can be used to modify the calculated behavior of nylon 12IA. The structure of nylon 12IA also presents an additional complexity with regard to nomenclature. It occupies a unique position in the table of aromatic polyamides in that it also contains aliphatic amide groups. Consequently, this polymer can be more accurately designated an $A_yB_zC''_{1-y-z}$ copolymer with calculated values of $y = 0.7514$, $z = 0.0476$, and $1 - y - z = 0.2010$. The quantities have been calculated by using the known distribution of diads, detailed earlier in the Experimental Section, and the group mer contribution to the molar volume of polymers.[21] Using the appropriate expression for χ_{blend} and the appropriate segmental interaction parameters produces a miscibility curve b as shown in Figure 10. Curve a represents a calculation based on the earlier more simple ABC nomenclature as drawn in Figure 1. As can be seen, a slight improvement is produced between the agreement of theory and experiment as listed in Table IV.

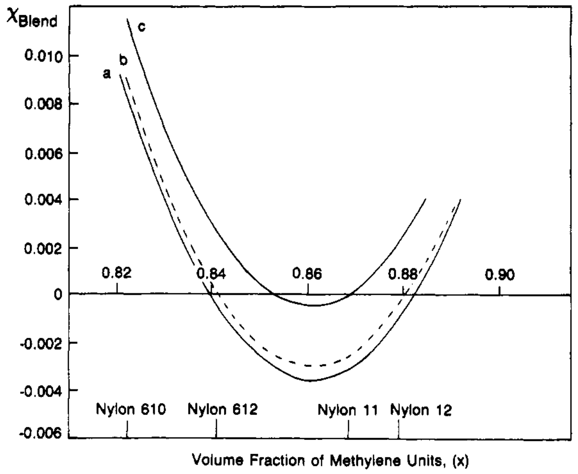


Figure 10. Calculated values of χ_{blend} of nylon 12IA in aliphatic polyamides: (a) as an $A_yB_zC_{1-y-z}$ copolymer, (b) correction applied for 1,3-phenyl isomer; $A_yB_zC''_{1-y-z}$ copolymer, (c) correction applied for alicyclic content; $A_yA'_{y'}B_zC''_{1-4y-y'-z}$ copolymer.

If small changes of structure, such as that presented by phenyl mer isomerism, produce changes in polymer solubility, then the introduction of alicyclic structures must also produce similar if not greater changes. This has always been recognized; however, only now is it possible to offer a semiquantitative explanation. If it is assumed that curve c, as shown in Figure 10, offers an accurate representation of experimentally observed behavior and differs from curve b because of the presence of alicyclic moieties, it should be possible to calculate the necessary segmental interaction parameters. When critical limits are used for x of 0.853 and 0.8685, respectively, and nylon 12IA is designated as an $A_yA'_{y'}B_zC''_{1-y-y'-z}$ copolymer, two equations have been established to solve for A'B and A'C'' (A' represents the alicyclic moiety). The critical limits chosen have been estimated entirely on the data presented in Table IV and are again established to produce the necessary symmetrical upward shift on the x axis.

Although the equation of χ_{blend} for mixtures of $A_xB_{1-x}/A_yA'_{y'}B_zC''_{1-y-y'-z}$ is quite simple in form, it is also rather voluminous and will not be reproduced here. The equation for χ_{blend} also contains a term associated with a $\chi_{AA'}$ interaction which is expected to be positive and small. Once again, as with the $\chi_{C'C''}$ term, there are insufficient boundary conditions available in order to solve for all the unknown segmental interaction parameters. If $\chi_{AA'}$ is assigned a zero value, then the values obtained for $\chi_{A'B}$ and $\chi_{A'C''}$ are as given in Table III.

The information generated thus far can be incorporated into a revision of the calculated behavior of nylon 6IcoTA. The projected behavior of this polymer when treated as an $A_yB_zC_{1-y-z}$ copolymer was shown in Figure 6 (curve a). Comparison of the experimental behavior given in Table VI with the calculated behavior produced a situation analogous to that observed for nylon 12IA. The critical limits calculated project a larger miscibility window than that actually observed; i.e., the calculated curve should be shifted upward in order to agree with experiment. In the more complex nomenclature developed thus far, nylon 6IcoTA is more realistically represented as a $A_yA'_{y'}C'_zC''_{1-y-y'-z}$ copolymer. Unfortunately the segmental interaction parameter $X_{A'C'}$ is not known; however, calculations based upon the polymer containing only 1,3-phenyl mers result in the curve given as b in Figure 6. This provides a more accurate representation of the experimental behavior even though nylon 610 is still predicted to be miscible, when in reality only partial miscibility ($\chi_{\text{blend}} \simeq 0$) was observed. Several additional qualifying comments should also be added with regard to the calculated behavior of nylon 6IcoTA. First, the alicyclic component of this polymer is slightly different from that used in nylon 12IA (see Table II). This may be partly responsible for the discrepancy between experiment and the new modified theory. Second, in order to perform a scrupulous calculation for χ_{blend}, blends of $A_xB_{1-x}/A_yA'_{y'}C'_zC''_{1-y-y'-z}$ copolymers require 10 segmental interaction parameters. Only seven of these have been shown to be available.

Conclusions

A binary interaction model has been found to provide a good description of phase behavior in polyamide blends containing aromatic polyamides that are substantially different in chemical composition from that upon which the model was originally founded. The initial calculations for all the blends described here were based upon parameters obtained from a previous analysis.[5] The observations reported have been used only to embellish the general model and to provide additional parameters to accurately reflect the structures contained in the aromatic polyamides described. This has resulted in four new segmental interaction parameters as shown in Table III. Thus, it can be seen that structural isomerism of the aromatic functionality introduces some changes in behavior, which can also be accounted for within the general scheme. However, the presence of alicyclic structures has been shown to have a much greater influence, and approximate calculations have been presented to show how this structural feature accounts for some of the experimental behavior.

The introduction of complex aromatic polyamides and the accompanying modifications made to accommodate these structures has required the imposition of a more fragmented, albeit no less real, nomenclature. While these developments are in one respect undesirable, they are also unavoidable given the nature of the polymers involved. However, the simple concepts embodied in the model still remain, and the more fragmented scheme offers some advantages over that employed previously. These new developments are able to offer an insight into the driving force for miscibility in blends of binary aromatic polyamides. The less refined model nomenclature is currently unable to describe miscibility in these blends, which has been shown to occur in several instances.[3] However, it is now possible to offer an explanation based upon an intramolecular repulsion effect, a feature that preserves the self-consistency of the model. This will be the subject of a future publication.[24]

Finally, it is worth noting once again that the sequential structure of the aliphatic polyamide is largely irrelevant when considering its solubility in the various aromatic polyamides. Only the overall chemical composition, i.e., the amide concentration, appears to be important in determining behavior. This is of particular concern for theories that prefer to explicitly involve hydrogen-bonding interactions as the driving force for miscibility within these blends and the concomitant configurational and conformational requirements that are usually considered vital to such theories.

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