the two chromophores into proximity and results in the formation of interchain aggregates at very low polymer concentration. Aggregates occur in water but not in alcohols or in a good solvent for HPC such as dioxane or methanol.

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Registry No. HPC, 9004-64-2.

References and Notes

(1) Just, E. K.; Majewicz, T. G. *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; Wiley: New York, 1985; Vol. 3, pp 226–269.
(2) See, for example: *Microdomains in Polymer Solutions*; Dubin, P., Ed.; Plenum: New York, 1985.
(3) Gelman, R. A.; Barth, H. G. In *Water-Soluble Polymers*; Glass, J. E., Ed.; ACS Symposium Series 213; American Chemical Society: Washington, DC, 1986; p 101.
(4) Winnik, F. M.; Winnik, M. A.; Tazuke, S.; Ober, C. K. *Macromolecules* **1987**, *20*, 38.
(5) Winnik, F. M. *Macromolecules* **1987**, *20*, 2745.
(6) Steinberg, I. Z. *Annu. Rev. Biochem.* **1971**, *40*, 83. Haas, E. In *Photophysical and Photochemical Tools in Polymer Science*; Winnik, M. A., Ed.; D. Reidel: Dordrecht, Holland, 1986; p 325.
(7) Morawetz, H. *Science (Washington, D.C.)* **1988**, *240*, 172.
(8) Morawetz, H. In *Photophysical and Photochemical Tools in Polymer Science*; Winnik, M. A., Ed.; D. Reidel: Dordrecht, Holland, 1986; p 547.
(9) Chang, L. P.; Morawetz, H. *Macromolecules* **1987**, *20*, 428. Miles, F.; Morawetz, H.; Dennis, K. S. *Macromolecules* **1980**, *13*, 969.
(10) Torkelson, J. M.; Gilbert, S. R. *Macromolecules* **1987**, *20*, 1860.
(11) Pekcan, O.; Winnik, M. A.; Egan, L. S.; Croucher, M. D. *Macromolecules* **1983**, *21*, 1011.
(12) Watanabe, A.; Matsuda, M. *Macromolecules* **1985**, *18*, 273; **1986**, *19*, 2253.
(13) Nagata, I.; Morawetz, H. *Macromolecules* **1981**, *14*, 87.
(14) Werbowyj, R. S.; Gray, D. G. *Macromolecules* **1984**, *17*, 1512.
(15) Nystrom, B.; Bergman, R. *Eur. Polym. J.* **1978**, *14*, 431.
(16) Gehra, E.; Sprizak, Y. *J. Am. Chem. Soc.* **1960**, *82*, 1915.
(17) *Dictionary of Organic Compounds*, 5th ed.; Buckingham, J., Ed.; Chapman and Hall: New York, 1983.
(18) Best yields and highest purity were obtained when the conditions described in the following reference for a general preparation of tosylates were followed: Kabalka, G. W.; Varma, M.; Varma, R. S.; Srivastava, P. C.; Knapp, F. F., Jr. *J. Org. Chem.* **1986**, *51*, 2386.
(19) Friedel, R. A. *Applied Spectrosc.* **1957**, *11*, 13.
(20) Martinho, J.; Egan, L. S.; Winnik, M. A. *Anal. Chem.* **1987**, *59*, 861.
(21) Rusakowicz, R.; Testa, A. C. *J. Phys. Chem.* **1968**, *72*, 2680.
(22) β-Elimination mechanisms of 9-fluorenylmethanol in aqueous solutions have been studied; see, for example: More O'Ferrall, R. A.; Slae, S. *J. Chem. Soc. B* **1970**, 260.
(23) (a) Berlman, I. B. *Handbook of Fluorescence Spectra of Aromatic Molecules*, 2nd ed.; Academic: New York, 1971. (b) Weber, G.; Teale, F. W. J. *Trans. Faraday Soc.* **1957**, *53*, 646.
(24) Yamazaki, I.; Winnik, F. M.; Winnik, M. A.; Tazuke, S. *J. Phys. Chem.* **1987**, *91*, 4213.
(25) Birks, J. B. *Photophysics of Aromatic Molecules*; Wiley-Interscience: London, 1970; Chapter 7.
(26) Georgelos, P. N.; Torkelson, J. M. *J. Non-Newtonian Fluid Mech.* **1988**, *27*, 191.
(27) (a) Nakajima, A. *J. Lumin.* **1977**, *15*, 277. (b) Dong, D. C.; Winnik, M. A. *Can. J. Chem.* **1985**, *62*, 2560.
(28) Saigusa, H.; Itoh, M. *J. Phys. Chem.* **1985**, *89*, 5486.
(29) Horrocks, D. L.; Brown, W. G. *Chem. Phys. Lett.* **1970**, *5*, 117.
(30) Minn, F. L.; Pinion, J. P.; Filipescu, N. *J. Phys. Chem.* **1971**, *75*, 1794.
(31) Förster, T. *Discuss. Faraday Soc.* **1959**, *27*, 7.
(32) Dexter, D. L. *J. Chem. Phys.* **1953**, *21*, 836.

Miscibility and Immiscibility of Polyamide Blends

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ABSTRACT: The solution behavior of blends of an amorphous aromatic polyamide, nylon 3Me6T, in a homologous series of aliphatic polyamides has been interpreted in terms of a recently introduced mean-field binary-interaction model. Founded on the premise that the polyamides in question can be treated as copolymers composed appropriately of methylene, amide, and phenyl mers, it has been possible to estimate the segmental interaction parameters, χ_{ij}. Using these values, a cartographic survey of the phase behavior of additional binary blends of aromatic/aliphatic polyamides has been conducted and found to correlate well with the experimental observations described here and in the literature.

Introduction

Although lacking in completeness, the Flory–Huggins approach[1,2] is often relied upon to provide a convenient and readily acceptable insight into the thermodynamics of polymer–polymer blends. The necessary negative Gibbs free energy of mixing, ΔG, is the primary requirement in order that two polymers are miscible. Additional prerequisites are also necessary; however, these restrictions are well understood to originate from the delicate balance between the entropic and enthalpic contributions to ΔG, although in the limit of high molar mass polymers, the entropic contribution is usually regarded to have a negligible impact upon the free energy balance. A further simplification, introduced by setting aside the free volume or equation of state contribution to ΔG, has shifted the focus of attention to the enthalpic term.[3] Accordingly it has been generally believed that a favorable or exothermic interaction between segments, or portions of segments, of different polymer species is the dominant factor promoting polymer–polymer miscibility.

Recent developments,[4–6] however, incorporating a mean-field binary interaction model, have shown that it is possible to accommodate the unusual phase behavior of blends of random copolymers by the inclusion of an unfavorable or repulsive interaction between the segments or mers comprising the copolymers. Essentially, this type of treatment assigns a segmental interaction parameter, χ_{ij}, to individual mers of each polymer and computes an overall value of the Flory interaction parameter, χ_{blend}, in order to predict phase behavior. This simple approach has been applied with great efficacy to account for a varied body of experimental observations.[7–14] Similarly it will also

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be shown to have equal applicability to the systems described here.

Previous communications[15,16] have presented a qualitative description of the solubility of an amorphous aromatic polyamide, denoted as nylon 3Me6T, in a homologous series of aliphatic polyamides, indicating that a region of miscibility was obtained bounded by an upper and a lower critical concentration of amide functionalities. The work presented here will demonstrate quantitatively the application and extension of the mean-field approach mentioned previously to these systems and to additional polyamide blends designed to test the validity of the results obtained. Such a treatment is of particular interest since alternative theories are available[17,18] which are directed specifically to blends containing polymers with polar functionalities capable of engaging in strong intermolecular interactions such as hydrogen bonding. Binary polyamide blends can be regarded as model examples of this category of blend and therefore would be considered to be unsuited to analysis founded upon a mean-field approach.[18] While it would certainly be of great interest to perform an analysis based upon these special theories, it will be shown that the experimental observations described here are also amenable to an interpretation based upon a mean-field prediction. Thus by treating the polyamides in question as copolymers, composed appropriately of methylene, amide, and phenyl mers, the theory allows for the calculation of the individual segmental interaction parameters, whose sign and magnitude, in conjunction with the relative abundance of each functionality, ultimately control the phase behavior of the blends. From the segmental interaction parameters calculated, a cartographic survey of binary blends based upon polyamides has been conducted, which in most instances will be shown to correlate with the experimental observations reported here and in the literature.

Theoretical Background

More complete descriptions of the thermodynamics of polymer–polymer solubility and the application of the mean-field binary interaction model can be found in the literature.[4–6] The relevant points and features will be reiterated here only to supply the essential narrative for the application of these theories to the systems described herein. As mentioned previously, it had always been generally accepted that in order for miscibility to occur between two polymers a favorable specific interaction had to exist between them. However, it has been noted on more than one occasion that blends containing a homopolymer and copolymer were miscible within certain ranges of copolymer composition even though blends with homopolymers of the monomers comprising the copolymer were immiscible. A so-called window of miscibility was obtained, which was related to an apparent mutual dislike between monomer units of the copolymer. Kambour et al.[4] recognized this repulsive effect between comonomer units within the copolymer as a potential driving force for miscibility. The expansion of this concept[5,6] also allowed the sensible interpretation of a large body of experimental data without invoking specific interactions. It has also been argued that such an approach overlooks the basic shortcomings of the simple Flory–Huggins model, especially when equation-of-state models provide a much more realistic description of how polymer blends behave in practice. These arguments, however, should not detract from the utility and self-consistency of the model.

Employing the formalism of the Flory–Huggins treatment of polymer–polymer solutions and following the spirit and notation of ten Brinke et al.,[5] it is possible to write the free energy balance of a mixing of two copolymers A_xB_{1-x} and C_yD_{1-y} as

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

where x and y represent copolymer compositions expressed as volume fractions of the individual mers of the copolymers of volume fractions ϕ_1 and ϕ_2. R is the gas constant, T is the absolute temperature, and N_1 and N_2 represent the degree of polymerization of polymers 1 and 2, respectively. The various χ_{ij}, as denoted by their subscripts, represent segmental interaction parameters. The first two terms of eq 1 approximate the combinational entropy of mixing which for high molar mass polymers can be considered to be negligible.

The essential feature of eq 1 is that the sign of the free energy of mixing, and hence phase behavior, is governed by the function shown by eq 2

$$f(\chi_{ij}) = [(1-x)y\chi_{BC} + xy\chi_{AC} + x(1-y)\chi_{AD} + (1-x)(1-y)\chi_{BD} - x(1-x)\chi_{AB} - y(1-y)\chi_{CD}] \quad (2)$$

where the overall phase behavior, predicted by χ_{blend}, is given by

$$\chi_{\text{blend}} = f(\chi_{ij}) - \chi_{\text{crit}} \quad (3)$$

The χ_{crit} term in eq 3 arises from the Flory–Huggins theory in the usual way[19] and is formulated as eq 4

$$\chi_{\text{crit}} = (N_1^{-1/2} + N_2^{-1/2})^2/2 \quad (4)$$

Thus, if the sum of all the terms in brackets in eq 2 is smaller than χ_{crit}, miscibility will result. Typically, for high molar mass polymers, χ_{crit} can be considered to be in the range 0.002–0.004 for $N_1 = N_2 \simeq 500\text{–}1000$. For the high molar mass polymers used in this study N_1 and N_2 can be considered large and χ_{crit} to be very small. For the following discussion χ_{crit} will be neglected. Therefore, χ_{blend} can be effectively represented by the quantities defined in eq 2. It should be stressed, however, that in blends where $\chi_{\text{blend}} \approx 0$, χ_{crit} can play a decisive role.

In the more simple cases for blends of a homopolymer and copolymer (A_x/C_yD_{1-y}) or blends of copolymers that differ only in composition (A_xB_{1-x}/A_yB_{1-y}), eq 5 and 6, respectively, obtain. An intriguing feature of the model

$$\chi_{\text{blend}} = xy\chi_{AC} + x(1-y)\chi_{AD} - y(1-y)\chi_{CD} \quad (5)$$

$$\chi_{\text{blend}} = (x-y)^2\chi_{AB} \quad (6)$$

is its ability to predict polymer miscibility, i.e., $\chi_{\text{blend}} < 0$, even though all individual segmental $\chi_{ij} > 0$. Alternatively it can be stated that miscibility can result between a homopolymer and a copolymer simply because of the fact that the individual mers comprising the copolymer have a greater repulsion for each other than the sum of the interaction between themselves and the mers comprising the homopolymer. The simplicity of the model requires a number of assumptions which are known not to be true and will obviously introduce some errors. The most important of these include that χ is independent of composition and that free volume effects are neglected.

The connectivity of mers is implicit within the model; however, the influence of a particular neighbor on an individual mer is not. From an alternative point of view, the model assumes that the interaction of the mers with each other is independent of their respective adjacent mers. This is obviously unrealistic and has formed the subject of several attempts to refine the basic model.[20,21] This facet of the model is especially important here since, as will become apparent later, the aliphatic polyamides can be

Table I
Material Characteristics and Properties

polymer	source	$10^{-3}M_n$	$10^{-3}M_w$	T_g, °C	T_m, °C
nylon 4	Chevron Research	150	471	59	267
nylon 46	Allied Chemical	22.3	100	58	291
nylon 6 (Zytel 211)	Du Pont	41	120	40	223
nylon 66 (Zytel 101)	Du Pont	31	92.5	45	262
nylon 69	Aldrich Chemical Co.	15	80.5	28	210
nylon 610	Aldrich Chemical Co.	12.5	87.5	25	222
nylon 612 (Zytel 151)	Du Pont	15	65.5	40	219
nylon 11 (Rilsan BMNO)	Rilsan Corp.	25	65	29	189
nylon 12 (Rilsan AESNO)	Rilsan Corp.	16	57	35	180
nylon 3Me6T (Trogamid T)	Kay Fries (Dynamit Nobel)	20	63	147	
nylon 6TcoT (Zytel 330)	Du Pont	14.1	49.8	127	
cycloaliphatic polyamide (Bexloy APC-803)	Du Pont			156	
polycaprolactone	Aldrich Chemical Co.			−60	58

Table II
Structure and Volume Fraction of Methylene Units (x) of Aliphatic Polyamides A_xB_{1-x}

poly-amide	structure	no. of CH_2 units/amide unit	x^a
nylon 4	$[-(CH_2)_3CONH]_n-$	3	0.6646
nylon 46	$[-(CH_2)_4NHCO(CH_2)_4CONH]_n-$	4	0.7255
nylon 6	$[-(CH_2)_5CONH]_n-$	5	0.7676
nylon 66	$[-(CH_2)_4CONH(CH_2)_6NHCO]_n-$	5	0.7676
nylon 69	$[-(CH_2)_6NHCO(CH_2)_7CONH]_n-$	6.5	0.8111
nylon 610	$[-(CH_2)_6NHCO(CH_2)_8CONH]_n-$	7	0.8222
nylon 612	$[-(CH_2)_6NHCO(CH_2)_{10}CONH]_n-$	8	0.8409
nylon 11	$[-(CH_2)_{10}CONH]_n-$	10	0.8685
nylon 12	$[-(CH_2)_{11}CONH]_n-$	11	0.8790

[a] Calculated by using group contributions given in Table IV.

considered to be random copolymers of amide and methylene functionalities; however, the aromatic polyamides in the strict sense should not be treated in the same way.

Experimental Section

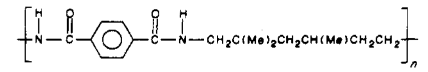
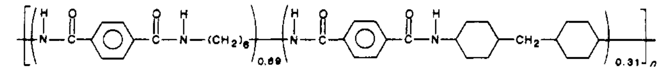
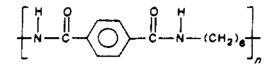
Materials. The sources, measured thermal properties, and molecular weight characteristics of the principal polymers incorporated into this study are summarized in Table I. Additional information describing their structure and composition is provided in Tables II and III, respectively. The structure of nylon 3Me6T (Trogamid T) has been idealized as the 2,2,4-trimethyl derivative; however, high-resolution NMR analysis has revealed the presence of additional isomers. Nevertheless, the ratio of aromatic to aliphatic protons was found to be in agreement with the structure given. Similar analysis of nylon 6IcoT confirmed the presence of the 1,6-hexanediamine and the presence of approximately 32 mol % of 1,4-substituted phenyl units, the remainder being composed of the 1,3-derivative. This contrasts with nylon 3Me6T which was found to contain exclusively the 1,4-phenyl derivative.

The amorphous cycloaliphatic polyamide, Bexloy AP C-803, is a commercially available material containing approximately 20% by weight of a phase-separated chemically bound rubber modifier. Its constituent polyamide is formed from the condensation of a stoichiometric composition of a mixture of 1,4- and 1,3-benzenedicarboxylic acids and a mixture of 1,6-hexanediamine and bis(4-aminocyclohexyl)methane.[22] NMR analysis of a filtered solution of the latter has confirmed that the ratio of the 1,6-hexanediamine to the cycloaliphatic diamine in 0.69:0.31. A similar ratio (1:2) of the 1,4-phenyl to the 1,3-phenyl derivative was found for this material as that obtained for nylon 6IcoT. Tables II and III also contain a summary of the volume fraction of the various chemical functionalities comprising the polymers, calculated by using group contributions[23] to the molar volume of polymers, as given in Table IV.

Blend Preparation. The salient details of blend preparation procedures are similar to those presented elsewhere;[15,16] however, a brief summary will be presented here. Unless stated otherwise, all blends were prepared at a composition of 50% by precipitation from a common solvent. In most cases a solvent system based on trifluoroethanol and methylene chloride (approximately 3:2 v/v) proved to be adequate. Typically a solution concentration of 2–3% by weight of polymer was found to be desirable, but for some blends containing nylon 11, nylon 12, and nylon 4 a higher dilution and heating was found to be necessary in order to produce clear solutions of a reasonable viscosity. In all cases diethyl ether was found to be an excellent precipitating medium. In some of the early stages of this work a solvent of 98% formic acid was used, and water was the precipitant. Solution blending of the rubber modified cycloaliphatic polyamide required filtration, in order to remove the rubber additive, prior to precipitation. Although this modifier is chemically bound to some of the polyamide, the exact blend composition was not expected to deviate significantly from that based on gravimetric determination prior to solvation. The filtered precipitate was washed extensively and dried under vacuum for 1 day at ambient conditions. In most cases, further drying was conducted under vacuum at approximately 50–60 °C.

Analytical Procedures. Thermal analysis was performed by using a Perkin-Elmer Model 7 Series differential scanning calorimeter (DSC) at a heating rate of 10 °C/min. Unless noted otherwise, values of the glass transition temperature, T_g, are reported as the onset of the transition and values for the melting point, T_m, are reported as the maximum of the melting endotherm. For experiments designed to determine the depression of T_m of a blend, a heating rate of 5 °C/min was employed, in order to reduce the possibility of superheating.

Table III
Structure and Composition of Amorphous Polyamides ($A_yB_zC_{1-y-z}$)

		vol fractn of methylene units^a y	vol fractn of amide units^a z	vol fractn of phenyl units^a $1-y-z$
nylon 3Me6T (Trogamid T)		0.5723	0.1915	0.2362
cycloaliphatic polyamide (Bexloy AP C-803)		0.5344	0.2085	0.2571
nylon 6IcoT (Zytel 330)		0.4702	0.2373	0.2925

[a] Calculated by using group contributions given in Table IV.

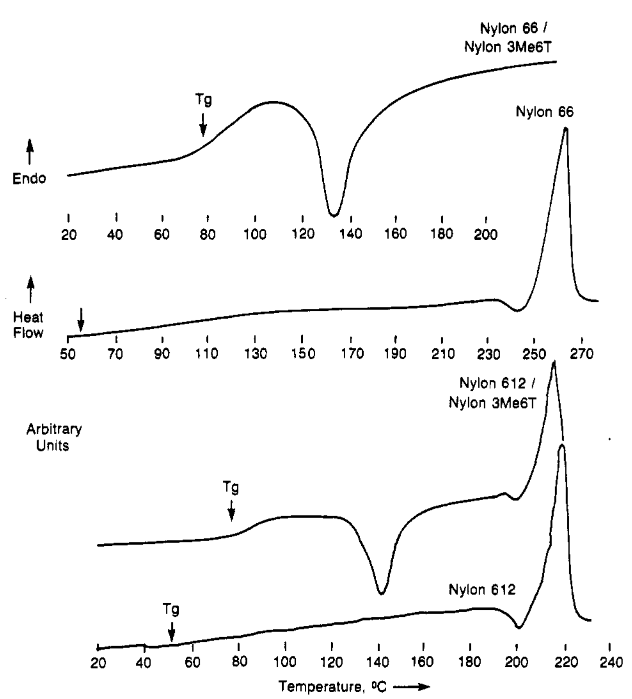


Figure 1. Representative thermograms of nylon 66, nylon 612, and their respective blends with nylon 3Me6T.

Table IV
Group Contributions to the Molar Volume of Polymers[a]

group	V_i, cm^3/mol	group	V_i, cm^3/mol
CH_2	16.45	C_6H_4 (disubstituted phenyl)	61.4
$CHCH_3$	32.65	CONH (amide)	24.9
$C(CH_3)_2$	50.35	C_6H_{10} (disubstituted cyclohexyl)	87.8

[a] Taken from ref 23.

Gel permeation chromatography (GPC) was conducted on solutions of the polymers in *m*-cresol at 110 °C by using a Waters Associates ALC chromatograph. The molecular weight averages, listed in Table I, were computed by using a universal calibration based upon polystyrene standards, and therefore the values should be viewed only for comparative purposes.

Results and Discussion

The Solubility of Nylon 3Me6T in Aliphatic Polyamides. It has already been reported[15,16] that nylon 3Me6T is soluble in nylons 6, 66, 69, 610, and 612 but insoluble in nylons 4, 46, 11, and 12. The experimental observations from which these conclusions are founded will be described in some detail here.

The criterion of a single composition-dependent T_g intermediate between that of the pure components is a well-known method of detecting miscibility.[2] Investigations of crystalline/amorphous polymer blends can also be augmented by scrutiny of additional phenomena such as the influence of a miscible additive on some measure of the crystallization kinetics of the crystalline component. In the instance of immiscibility occurring, measurement of the incremental change in heat capacity (ΔC_p) at T_g can also be of assistance. All of these criteria was implemented to establish without ambiguity the phase behavior of nylon 3Me6T in the semicrystalline polyamides. Because of the sometimes subjective nature of thermal analysis, examples of the behavior of some of the blends are shown in Figures 1 and 2. The thermograms shown in Figure 1 illustrate the miscibility of nylon 3Me6T in nylons 66 and 612. The amorphous (quench cooled) blends demonstrate a T_g intermediate between those of the pure polymers, together with a major reduction of the rate of crystallization on further heating. This was manifested by changes of the crystallization exotherm. Identical behavior has been observed for blends of nylon 3Me6T and nylons 6, 69, and 610.

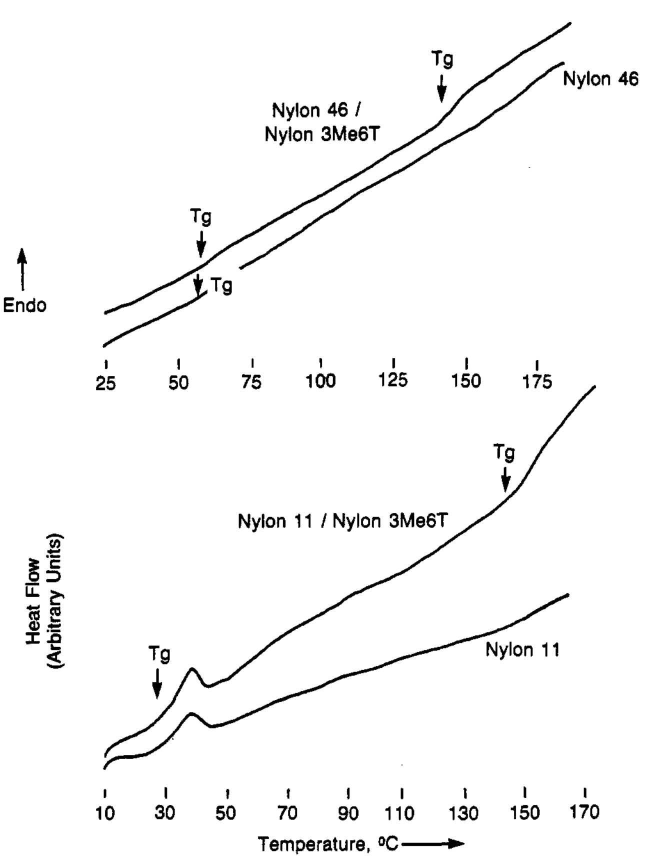


Figure 2. Representative thermograms of nylon 46, nylon 11, and their respective blends with nylon 3Me6T.

Quench-cooled samples of some of the pure aliphatic polyamides were still capable of crystallizing at a sufficiently rapid rate during the quenching process to produce a material containing an extensive amount of crystallinity. Therefore the thermograms, shown in Figure 1, of quench-cooled samples of nylon 66 and nylon 612, exhibit no crystallization exotherm and a very small change of ΔC_p at T_g. Indeed, from the thermograms shown, it is difficult to detect the T_g; however, close inspection at a higher sensitivity does reveal an unmistakable change of heat capacity at the points indicated.

The thermograms presented in Figure 2 illustrate the immiscibility of nylon 3Me6T when blended with nylons 46 and 11. In both cases heat capacity changes associated with the T_g's of the amorphous nylon component and the respective aliphatic polyamide are clearly visible. Measurements of the ΔC_p of nylon 3Me6T in the blends were in close agreement with that recorded for the pure polymer ($\simeq$0.39 J/g·K). Similarly the position of the T_g of the semicrystalline polymer appears to be unaffected by the presence of the nylon 3Me6T component and there is no visible influence upon the crystallization behavior of the aliphatic polyamide in the quench-cooled blends. These observations were also obtained for blends containing nylons 4 and 12 and support the conclusion of immiscibility. The solution behavior of nylon 3Me6T in the semicrystalline polyamides, together with a summary of the measured values of T_g, is given in Table V. The composition-dependent T_g of miscible polymer blends rarely follows true linear additivity. This was found to be particularly true for the nylon 6/nylon 3Me6T blend,[15,16] where a strong concave dependence was observed. There

Table V
Thermal Properties and Phase Behavior of Nylon 3Me6T/Aliphatic Polyamide Blends

blend component (T_g, °C)	T_g of 50:50 blend,[a] °C	obsd blend soln behavior	calcd χ_{blend}[b]
nylon 4 (59)	65, 143	2 T_g's, immiscible	0.0400
nylon 46 (58)	58, 143	2 T_g's, immiscible	0.0065
nylon 6 (40)	75	1 T_g, miscible	−0.0050
nylon 66 (45)	74	1 T_g, miscible	−0.0050
nylon 69 (28)	77	1 T_g, miscible	−0.0069
nylon 610 (25)	75	1 T_g, miscible	−0.0058
nylon 612 (45)	71	1 T_g, miscible	−0.0023
nylon 11 (29)	29, 144	2 T_g's, immiscible	0.0061
nylon 12 (35)	39, 144	2 T_g's, immiscible	0.0104

[a] Nylon 3Me6T, T_g = 147 °C. [b] Calculated by using eq 7.

are sound reasons for this type of behavior; however, it is worthwhile noting that all the miscible blends mentioned in this paper appear to behave in a similar manner. This is exemplified in Table V where the single T_g of the miscible polymer blends was found to be well below that of the value representative of linear additivity. There are two important aspects of the determination of phase behavior which require qualification before proceeding further. These are the effects of thermal stability and critical solution phenomena.

Transreaction is an established feature of blends of polycondensation polymers.[24] In the experiments described here, the minimal level of thermal exposure prior to establishing the phase behavior of all the blends investigated would tend to negate its importance as a factor in the observed miscibility of any of the blends. Nylon 4, however, is known to have problems related to thermal stability in the melt.[25] Therefore, the phase behavior of the blend was established both prior to (235 °C) and after melting at 275 °C for 1 min. No significant differences were detected, implying that degradation of the nylon 4 was not a factor in the phase behavior observed.

In all the blends investigated there was no indication of the presence of phase separation, in the form of a lower critical solution temperature (LCST) or partial miscibility. However, the phase behavior was established on blends, mostly in the amorphous state, produced by quench cooling from the melt. This was a mandatory requirement since the blend produced by coprecipitation is in a nonequilibrium state containing a mixed amorphous phase and a crystalline phase. Under these circumstances, melting of the blend is the only procedure capable of rendering a homogeneous equilibrium state. Phase separation can of course occur only above the respective T_g; therefore there is a potential for an LCST to occur somewhere between T_g and T_m. For blends containing low melting point nylons, e.g., 11 and 12, this temperature difference is small and an LCST would be difficult to detect. Blends containing nylons 4 and 46, high melting temperature nylons, were subjected to heating cycles below the melt temperature in order to establish phase behavior prior to melting. In the case of nylon 4, no LCST was observed and two phases could be detected.

Application of the Model to Nylon 3Me6T/Aliphatic Polyamide Blends. It is possible to treat the aliphatic polyamides as a homologous series of copolymers, A_xB_{1-x}, containing methylene and amide mers, where A represents a methylene unit and B represents an amide unit. The value of x represents the volume fraction of methylene units comprising the copolymer. Use of group contributions to the molar volume of polymers,[23] as given in Table IV, allows for the calculation of x for all the aliphatic polyamides that are also recorded in Table II. An aromatic polyamide such as nylon 3Me6T can equally be represented as a copolymer of methylene, amide, and phenyl mers, $A_yB_zC_{1-y-z}$, in which y and z can also be calculated, as shown in Table III. At this point a simplification has to be introduced. In the case of nylon 3Me6T, it will be assumed that methyl groups interact in the same way as a methylene group. At first inspection this does not appear to be an unreasonable assumption.

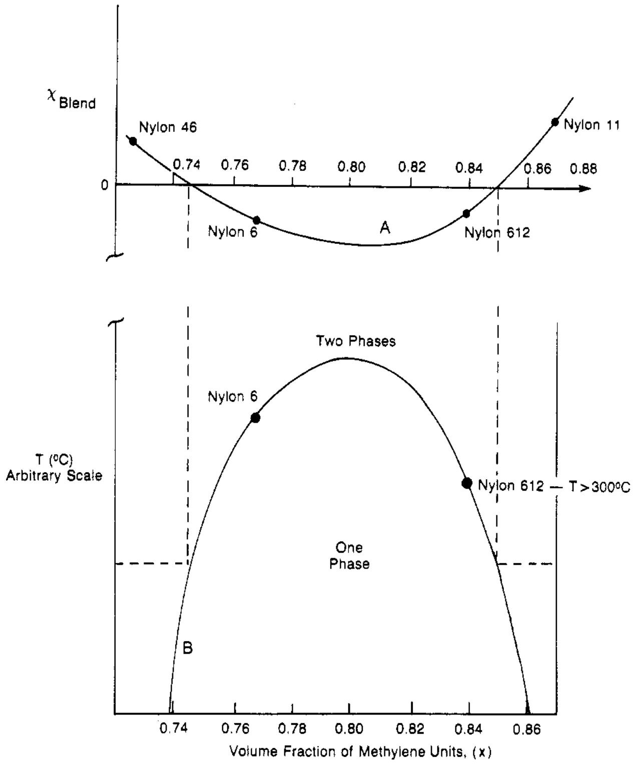


Figure 3. Schematic illustration of phase behavior (curve A) of nylon 3Me6T in aliphatic polyamides (A_xB_{1-x}); curve B defines the locus of LCST's.

From the experimental evidence presented above it is possible to sketch a diagram, as shown in Figure 3, of the behavior observed. The top section of the figure describes qualitatively the form of χ_{blend} as a function of the volume fraction of methylene units (x) of the aliphatic polyamide (curve A). When χ_{blend} is positive, immiscibility occurs, and the converse is true when χ_{blend} is negative. The scheme presented provides for the existence of two crossover points where $\chi_{blend} = 0$. The lower part of Figure 3, curve B, defines the locus of lower critical solution temperatures for the blends. The LCST denotes the temperature at which a blend moves from a miscible one-phase regime to a two-phase region as noted in the figure. This figure explains qualitatively why no phase separation phenomena was observed in the temperature range up to 300 °C. In general, χ_{blend} is an increasing function of temperature such that χ_{blend} of blends containing nylons 6 and 612, respectively, must be sufficiently negative that an LCST does not occur within the temperature range of observation. Similarly nylons 46 and 11, respectively, must have a χ_{blend} sufficiently positive that an LCST also does not occur below their respective T_m. These features will play an important role in later calculations, as will be described subsequently.

Following the notation of ten Brinke et al.[5] it is trivial to show that for a blend of the polymers A_xB_{1-x} and $A_yB_zC_{1-y-z}$ eq 2 and 3 can be rewritten as eq 7

$$\chi_{blend} = [(1-x)(y-x) + z(x-y)]\chi_{AB} + (1-y-z)(1-x-z)\chi_{BC} + (1-y-z)(x-y)\chi_{AC} \quad (7)$$

It is quite straightforward to reduce this expression to the simple cases resulting in eq 5 and 6 by applying the necessary nomenclature. Thus eq 7 reduces to an equation equivalent to (5) for a mixture of a homopolymer A (x = 1) with that of a copolymer B_zC_{1-z} (y = 0). Similarly eq 7 reduces to eq 6 for a mixture of two copolymers that differ only in comonomer composition, A_xB_{1-x} and A_yB_{1-y} ($C = 0$, $z = (1 - y)$).

Inspection of eq 7 indicates that if the three segmental interaction parameters χ_{AB}, χ_{BC}, and χ_{AC} are known, then the overall quantity χ_{blend} can be determined. In summary, three linear equations have to be defined in order to solve for the three unknowns. Rearrangement of eq 7 also shows χ_{blend} to be a quadratic function of x and therefore the equation satisfies the qualitative schematic shown in Figure 3.

From experimental observations summarized in Table V, it is possible to set an upper bound and a lower bound, where $\chi_{blend} = 0$, at the points for the two copolymer compositions $0.7255 < x < 0.7676$ and $0.8409 < x < 0.8685$. These two points represent the copolymers where nylon 3Me6T changes from an immiscible to a miscible component. The third equation, necessary for solving to obtain χ_{AB}, χ_{BC}, and χ_{AC}, can in principle be established from a melting point depression analysis of nylon 3Me6T in nylon 6. The known temperature dependence of the interaction parameter, taken in conjunction with the latter condition, will impose a reference temperature equal to the equilibrium melting point of nylon 6.

The preceding text requires some commentary with regard to the choice of subdivision of the polymer chain to define the constituent mers. An equally realistic designation of constituent mers can be formulated by considering the aliphatic polyamides to be composed of methylene ($-CH_2-$) and methylene-substituted amide ($CH_2NHCOCH_2$) mers. Similarly the aromatic polyamide can be considered to be composed of methylene- and amide-substituted phenyl (NHCOPhCONH) mers. With these assignments the blend becomes a mixture of $A_xB'_{1-x}$ and $A_yC'_{1-y}$ copolymer and eq 7 reduces to

$$\chi_{blend} = (y - x)(1 - x)\chi_{AB} + (1 - y)(1 - x)X_{B'C'} + (x - y)(1 - y)\chi_{AC'} \quad (8)$$

There are of course three unknown segmental interaction parameters as before but the expression for χ_{blend} has been simplified. In a sense the latter treatment has more validity in that the amide groups of the amorphous polyamide remain in the configuration given as C′; i.e., the situations $-CH_2NHCOCH_2$ and $-CH_2PhCONH$ do not occur within this polymer. In other words, nylon 3Me6T is not a true random copolymer of amide, methylene, and phenyl functionalitieis. However, the assigned classification of nylon 3Me6T as an $A_yB_zC_{1-y-z}$ copolymer will be maintained, since this type of mer subdivision is less restrictive. As a corollary, however, additional cognizance must be made of the fact that the interaction of the phenyl unit will be influenced by its environment and that it cannot be assumed, for example, that a χ_{AC} interaction is representative of that encountered in, for example in a polyethylene/polystyrene blend.

Depression of the Melting Point of Nylon 6 by Nylon 3Me6T. The application[26] of work by Flory[27] to the analysis of the melting point depression of a polymer by a second miscible amorphous polymer is a well-known method for the evaluation of the interaction parameter. The most simple expression to represent the depression of T_m by a miscible polymeric additive is given as

$$\frac{1}{T_m{}^0{}_{blend}} - \frac{1}{T_m{}^0} = -\frac{RV_2}{\Delta h_2 V_1}\chi_{12}(1 - \phi_2)^2 \quad (9)$$

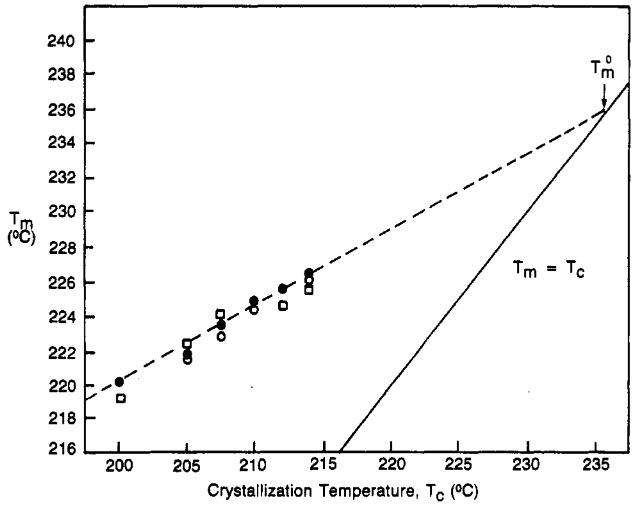


Figure 4. Melting point of nylon 6/nylon 3Me6T blends crystallized above 200 °C: (●) nylon 6; (□) 25% w/w nylon 3Me6T; (○) 50% w/w nylon 3Me6T.

By ignoring entropic contributions to χ_{12}, it is possible to write

$$\chi_{12} = BV_1/RT \quad (10)$$

where B is the interaction energy density. Combining eq 9 and 10 and putting $T = T_m{}^0{}_{blend}$ it is possible to write

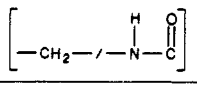
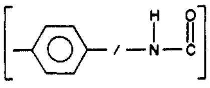
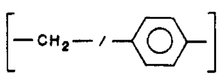
$$(1 - T_m{}^0{}_{blend}/T_m{}^0) = \frac{-BV_2}{\Delta h_2}(1 - \phi_2)^2 \quad (11)$$

In these equations $T_m{}^0$ and $T_m{}^0{}_{blend}$ are the equilibrium melting points of the crystallizable component in the pure state and the blend, respectively, R is the gas constant, V_i is the molar volume of the respective component, Δh_2 is the heat of fusion per mole of repeat unit, and ϕ_2 is the volume fraction of component 2 present in the blend. If values of $T_m{}^0$ and $T_m{}^0{}_{blend}$ are obtained, a suitable graphical procedure facilitates an estimation of B and therefore χ_{12}, i.e., χ_{blend}.

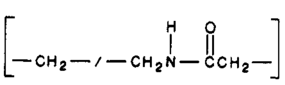
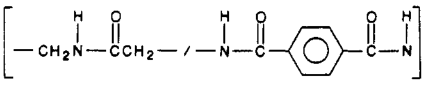
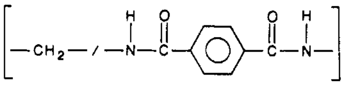
From the work of Hoffman and Weeks,[28] the equilibrium melting points can be determined from isothermal crystallization experiments by extrapolation of the measured T_m to the point where $T_m = T_c$, where T_c is the crystallization temperature. Previous observations[16] have already highlighted some of the difficulties with these experiments for nylon 6 and its blends. Isothermal crystallization has to be effected at temperatures above 200 °C, a temperature regime where the rate of crystallization is very slow. This practical drawback was compounded in the blends by the presence of nylon 3Me6T which reduces the rate of crystallization even further. Despite these shortcomings, it was possible to measure values of T_m for materials crystallized up to 214 °C for 18 h as shown in Figure 4. The equilibrium melting point of nylon 6 was estimated to be 236.0 °C, a value in good agreement with previous findings.[29] It is difficult from the data presented in Figure 4 to establish any reliable or meaningful estimates of the depression of the melting point in any of the blends. This observation signifies that χ_{blend} for nylon 6/nylon 3Me6T at approximately 236 °C is probably very small. This conclusion can be supported by numerical analysis using eq 9. For the value of $\chi_{12} = -0.01$ the depression of melting point for the blend at $\phi_2 = 0.5$ would be approximately 0.1 K. It is therefore not surprising that such small values of depression of T_m produced insignificant variations of the slopes of the T_m versus T_c plots as shown in Figure 4. It is apparent from the foregoing that an accurate determi-

Table VI
Calculated Values of the Segmental Interaction Parameters χ_{ij}

Blend of $A_xB_{1-x}/A_yB_zC_{1-y-z}$

nylon 6/nylon 3Me6T χ_{blend}	 $\left[-\mathrm{CH_2}-/-\overset{\mathrm{H}}{\mathrm{N}}-\overset{\mathrm{O}}{\mathrm{C}}\right]$		
−0.002	1.074	0.923	−0.051
−0.005	2.685	2.308	−0.127
−0.01	5.370	4.616	−0.254

Blend of $A_xB'_{1-x}/A_yC'_{1-y}$

nylon 6/nylon 3Me6T χ_{blend}	 $\left[-\mathrm{CH_2}-/-\mathrm{CH_2}\overset{\mathrm{H}}{\mathrm{N}}-\overset{\mathrm{O}}{\mathrm{C}}\mathrm{CH_2}-\right]$		
−0.002	0.199	−0.0142	0.224
−0.005	0.498	−0.0355	0.561
−0.01	0.996	−0.0711	1.122

nation of χ_{blend}, for the nylon 6/nylon 3Me6T system, is not attainable from the data obtained from a melting point depression approach.

Estimation of the Segmental Interaction Parameters. As described previously, three equations are required in order to solve for the three segmental interaction parameters. The foregoing discussion has demonstrated the difficulty in formulating these equations with the desired accuracy. It is possible, however, to make suitable approximations based on a number of factors as follows.

Values of χ_{blend} for nylon 6/nylon 3Me6T were arbitrarily set at −0.002, −0.005, and −0.01, establishing three separate equations for this particular blend. For each of these equations two additional equations were formulated such that $\chi_{\mathrm{blend}} = 0$. Values of x were fixed by a semiempirical iteration procedure and by taking into account that no LCST behavior had been observed in the blends. For each fixed point where $\chi_{\mathrm{blend}} = 0$, there is a lower and an upper limit as defined previously. Selecting values of x too close to these limits can result in values of χ_{blend} for a known miscible blend pair to be close to zero. In such an instance it may be expected that an LCST could be observed, which as mentioned previously could not be detected experimentally. In the other extreme, values of χ_{blend} for known immiscible blends can be close to zero where χ_{crit} may have an influence, suggesting that a miscible blend should have been observed.

An additional important factor in determining the two values of x where $\chi_{\mathrm{blend}} = 0$ was provided by the results of the solution behavior of a second amorphous polyamide, nylon 6IcoT, in the same series of aliphatic polyamides. The results of these studies will be described subsequently; however, in essence the values of x chosen here also had to compute values of χ_{blend} which were consistent with the behavior of nylon 6IcoT. In summary, the values of x chosen for $\chi_{\mathrm{blend}} = 0$ had to provide values of the segmental interaction parameters which, when applied to blends of nylon 6IcoT, gave values of χ_{blend} which were negative for a blend containing nylon 69 and positive for a blend containing nylon 610. This would then provide qualitative agreement with experimental observations which had indicated the amorphous polyamide to form a miscible blend with nylon 69 and an immiscible blend with nylon 610. By taking all of these factors into consideration, the lower bound and upper bound of x were fixed at 0.745 and 0.85, respectively. Interestingly, these two values are almost intermediate between their respective limits as defined previously ($0.7255 < x < 0.7676$ and $0.8409 < x < 0.8685$).

Combining the two equations established for $\chi_{\mathrm{blend}} = 0$ and the three equations for χ_{blend} of nylon 6/nylon 3Me6T when $\chi_{\mathrm{blend}} = -0.002, -0.005$, and -0.01 allows three curves to be constructed, illustrating quantitatively the dependence of χ_{blend} upon x. The three curves, as shown in Figure 5, all agree with the phase behavior observed for these systems, and the values of χ_{ij} used to construct these curves are given in Table VI. Identical curves can be constructed if the alternative description of mer assignment is invoked as described previously, whereby the blended polymers are treated as $A_xB'_{1-x}/A_yC'_{1-y}$ copolymers. As may be expected when using this nomenclature, the only quantities that differ are the calculated values of the segmental interaction parameters. These values are also given in Table VI.

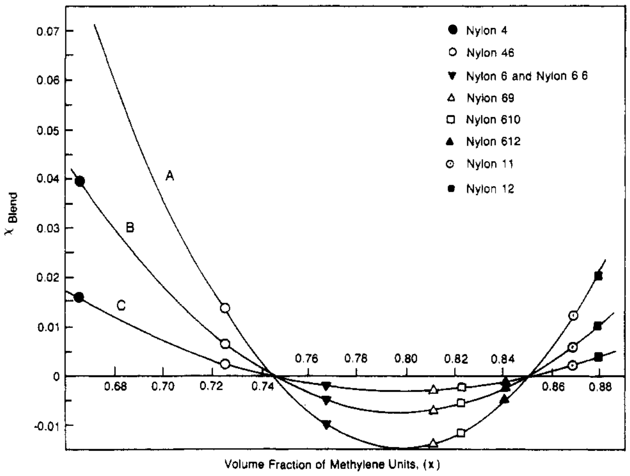


Figure 5. Calculated values of χ_{blend} of aliphatic polyamide (A_xB_{1-x})/nylon 3Me6T blends when χ_{blend} of nylon 6/nylon 3Me6T was set at −0.01 (A), −0.005 (B), and −0.002 (C).

At this point it would be beneficial to review several features and trends which require special considerations and comment. The magnitude of χ_{blend} chosen for the nylon 6/nylon 3Me6T blend controls the obliqueness of the curve generated and in turn the magnitude of the segmental interaction parameters. However, when $\chi_{\mathrm{blend}} = -0.002$ the values of χ_{blend} for blends containing nylon 46 and nylon 11 are 0.0026 and 0.0024, respectively. These blends, as stated previously, have been shown to be immiscible and such small values of χ_{blend} would tend to suggest that for nylon 6 the case where $\chi = -0.005$ may be a more realistic value. It may be argued that when χ_{blend} for nylon 6 is −0.01 the values obtained for χ_{AB} and χ_{AC} (see Table VI) become excessively large. From all these values of χ_{ij}, the qualitative picture does not change at all; only the quantitative values change such that the role of χ_{blend} of the nylon 6/nylon 3Me6T blend is simply that of a scaling factor.

Large segmental interaction parameters have been obtained from the similar analysis of other polymer blends.[10,13] The physical basis of such a large, positive interaction between amide and methylene and amide and phenyl units, respectively, can be understood within the context of their chemical nature. An amide group is a strong polar hydrophilic functionality in almost any chemical environment. Conversely the methylene and phenyl functionalities can be considered the direct opposite, and therefore it is perhaps not surprising that a large positive value of the segmental interaction parameter has been obtained. The slightly negative, and therefore favorable, interaction between the methylene and phenyl units is more difficult to qualify; however, it is probably attributable to the chemical environment of the phenyl unit, which has two adjacent amide functionalities. It follows from this that the phenyl/methylene interaction calculated here is only applicable when they are in the configuration provided by the polyamide environment. If the value was representative of all methylene and phenyl interactions then polystyrene would be miscible with polyethylene, which it clearly is not.[1]

It is of interest to note that the alternative analysis of the copolymer blend resulting in the segmental interaction parameters $\chi_{AB'}$, $\chi_{B'C'}$, and $\chi_{AC'}$ as shown in Table VI results in much more moderate values. This result also has a sound physical basis, which in this instance is related to the way in which copolymer status was assigned to the polyamides. The value of χ_{blend} for any polymer blend is usually small and representative of the overall interaction of two different polymer molecules. In this type of approach, where the individual mers are chemically distinct, the values of χ_{ij} may be extreme. If the individual mers become less distinct, then the individual χ_{ij} will approximate more closely to that of the complete polymer molecule. As a corollary, much larger values of χ_{ij} are conceivable if the individual mers are capable of being subdivided even further, e.g., by splitting the amide functionally into —NH and —C═O units.

Except for using the known phase behavior of nylon 6IcoT in nylon 69 and nylon 610 to assist in establishing the value for the upper bound value of x, the phase behavior of nylon 3Me6T in the homologous series of aliphatic polyamides has been quantitatively accounted for independent of any additional considerations. We shall now see how the calculated values of χ_{ij} can be used to account for the behavior of a wide variety of polyamide binary blends.

The Solubility of Nylon 6IcoT in the Aliphatic Polyamides. The phase behavior of nylon 6IcoT in the semicrystalline polyamides was assessed in an identical manner to that describe for nylon 3Me6T. This was achieved by employing the same criteria of a single composition-dependent T_g, the retarding influence of a miscible, higher T_g, polymeric additive on the crystallization processes of the aliphatic polyamide, and measurements of heat capacity changes, ΔC_p, associated with T_g.

The thermogram of the blend of nylon 6IcoT and nylon 69, when compared to that obtained from pure nylon 69 as shown in Figure 6, illustrates a single T_g between that of the two pure components together with perceptible retardation of the crystallization exotherm on further heating above T_g. In contrast to this observation, a 50:50 blend containing nylon 610 appears to indicate complete immiscibility as noted by the presence of two T_g's similar to those of the pure polymers. This behavior is also illustrated in Figure 6 and is analogous to that obtained for nylon 3Me6T based blends. The blends containing nylon 6IcoT also revealed the presence of two compositions at which the volume fraction of methylene units, x, of the aliphatic polyamide provided a critical concentration ($\chi_{\text{blend}} = 0$), such that the amorphous polyamide was transformed from an immiscible to a miscible component. As mentioned previously, the first point when $\chi_{\text{blend}} = 0$ resides between the values of x for nylon 69 and nylon 610 ($0.8111 < x < 0.8222$), and from these studies it is apparent that the lower of these critical concentrations is intermediate between that of nylon 4 and nylon 46 ($0.6646 < x < 0.7255$). Evidence for this conclusion is provided in Figure 7. The thermogram shown for the blend containing nylon 46 is that obtained from a quench-cooled blend containing 75% by weight of nylon 6IcoT. At this composition, unlike that obtained for a 50:50 blend, the additional retarding influence of the amorphous polymer on the crystallization behavior of the nylon 46 could also be observed. Both the

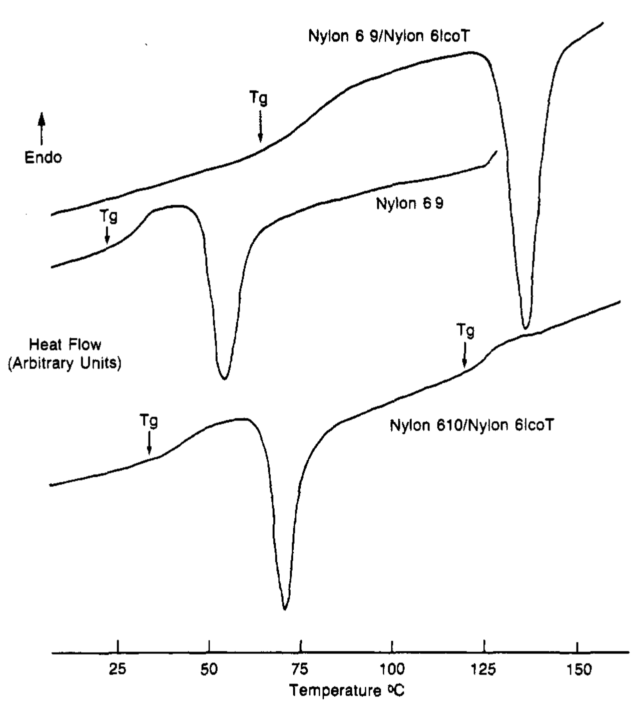


Figure 6. Representative thermograms of nylon 69 and blends of nylon 69 and nylon 610 containing nylon 6IcoT.

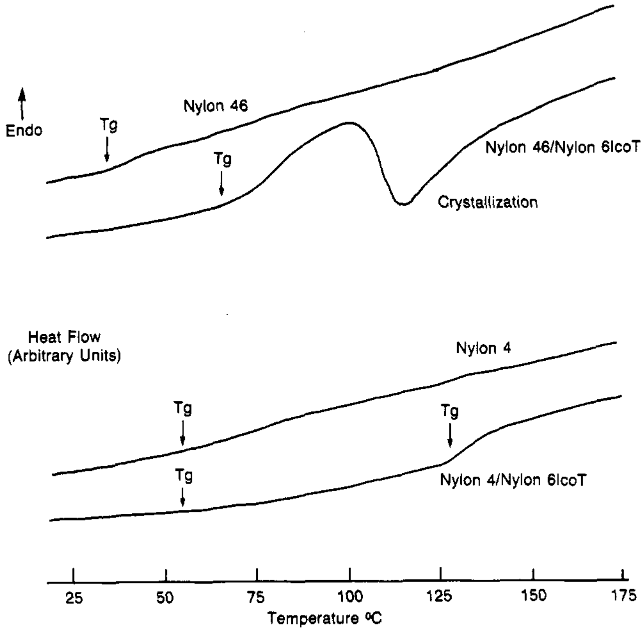


Figure 7. Representative thermograms of nylon 4, nylon 46, and their respective blends containing nylon 6IcoT.

Table VII
Thermal Properties and Phase Behavior of Nylon 6IcoT/Aliphatic Polyamide Blends

blend component (T_g, °C)	T_g of 50:50 blend,[a] °C	obsd blend solution behavior	calcd χ_{Blend}[d]
nylon 4 (59)	≃65, 127	2 T_g's, immiscible	0.0078
nylon 46 (58)	77, 93[b]	1 T_g, miscible	-0.0099
nylon 6 (40)	71	1 T_g, miscible	-0.0104
nylon 66 (45)	70,[c] 90[b]	1 T_g, miscible	-0.0104
nylon 69 (28)	63	1 T_g, miscible	-0.0010
nylon 610 (25)	35, 127	2 T_g's, immiscible	0.0030
nylon 612 (45)	38, 127	2 T_g's, immiscible	0.0113
nylon 11 (29)		not investigated	0.0269
nylon 12 (35)		not investigated	0.0340

[a] Nylon 6IcoT T_g = 127 °C. [b] Blend containing 75% by weight of nylon 6IcoT. [c] Blend containing 32% by weight of nylon 6IcoT. [d] Calculated by using eq 7.

50% and 75% by weight blends gave a single T_g intermediate between those observed for the pure components. To contrast with this behavior, a blend of nylon 6IcoT and nylon 4 displayed a thermogram, as shown in Figure 7, consistent with the formation of an immiscible system.

Blends of nylon 6IcoT with nylon 6 and nylon 66 were also found to exhibit thermal properties completely in accord with the formation of a miscible system. As expected, however, a blend of the amorphous polymer and nylon 612 was found to be immiscible. Blends of nylon 6IcoT and nylon 11 and nylon 12 were not investigated but on the basis of previous findings are expected to be immiscible. A summary of thermal properties and phase behavior of the blends investigated is shown in Table VII. In some instances, there are some slight discrepancies between the T_g's of the pure aliphatic polyamide and that recorded for the same polymer in an immiscible blend. This was usually the result of the difficulties associated with the accurate estimation of T_g owing to the very small heat capacity changes associated with the transition in a semicrystalline polymer. The blend of nylon 6IcoT with nylon 610 provided some evidence of partial or limited miscibility. This was noted by a slightly increased T_g of tne nylon 610 in the blend, as recorded in Table VII, over that measured for the pure polymer. In addition to this, and in contrast to the pure nylon 610, it was also possible to quench cool the blended nylon 610 and produce a crystallization exotherm on subsequent analysis as shown in Figure 6. It will be shown that these observations are in qualitative agreement with a calculated value of χ_{blend} which is only slightly positive ($\chi_{\text{blend}} \simeq 0.003$).

Application of the Model to Nylon 6IcoT/Aliphatic Polyamide Blends. Although a critical feature of these calculations, the arbitrary choice of $\chi_{\text{blend}} = -0.005$ for the nylon 6/nylon 3Me6T blend has allowed for an estimation of the segmental interaction parameters, $\chi_{\text{AB}} = 2.685$, $\chi_{\text{BC}} = 2.308$, and $\chi_{\text{AC}} = -0.127$. Using these values of χ_{ij} and eq 7, it is also possible to provide a quantitative description of the phase behavior of nylon 6IcoT in the aliphatic polyamides. In order to do so, it also has to be assumed that nylon 6IcoT can also be denoted as a $A_yB_zC_{1-y-z}$ copolymer. More importantly, however, it now has to be assumed that a 1,3-substituted phenyl mer interacts in the same way as a 1,4-substituted phenyl mer. While this may seem to be a reasonable simplification, it has been found that structural isomerism of a substituted phenyl nucleus produces small variations of the segmental interaction parameter, which are sensitive to the position at which substitution occurs.[5,7]

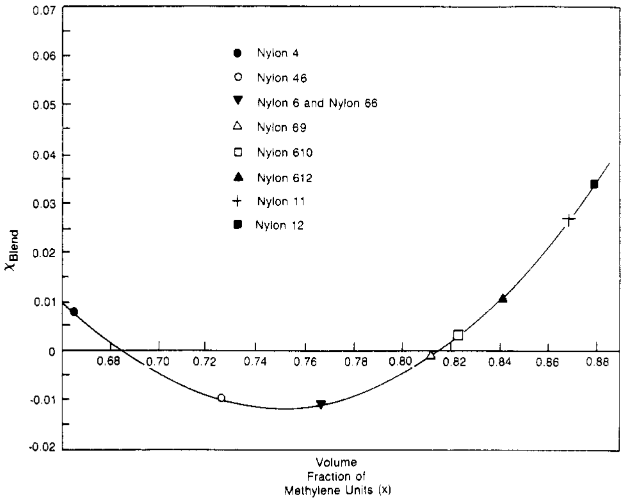


Figure 8. Calculated values of χ_{blend} of aliphatic polyamide (A_xB_{1-x})/nylon 6IcoT blends.

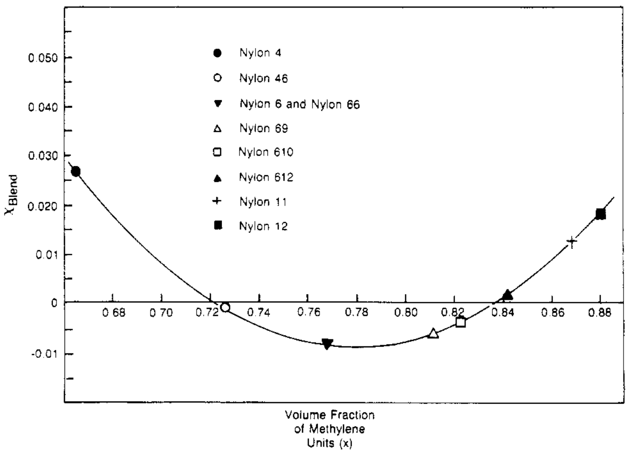


Figure 9. Calculated values of χ_{blend} of aliphatic polyamide (A_xB_{1-x})/cycloaliphatic polyamide blends.

The calculated curve of χ_{blend} as a function of aliphatic polyamide composition for blends containing nylon 6IcoT is shown in Figure 8. The calculated values are also listed in Table VII. The upper bound for the volume fraction of methylene units obviously lies between that of nylon 69 and nylon 610. However, theory predicts nylon 6IcoT to be miscible with nylon 46, which is a sharp contrast to that observed for nylon 3Me6T, despite their close chemical similarity. As noted previously, the experimental observations confirm these predictions. The theory shows that nylon 11 and nylon 12 should also be immiscible with nylon 6IcoT, a prediction which has not yet been verified.

Application of the Model to Additional Polyamide Blends. Cycloaliphatic Amorphous Polyamide. The amorphous cycloaliphatic polyamide is a chemically complex material formed form a mixture of iso- and terephthalic acids, 1,6-hexanediamine, and a bis(4-aminocyclohexyl)methane derivative. Despite this complexity, it is still possible to treat this material as an $A_yB_zC_{1-y-z}$ copolymer if it is assumed that the component methylenes of the bis(4-aminocyclohexyl)methane unit interact in the same manner as a single methylene unit contained in the polyalkylene chain of nylon 6IcoT and nylon 3Me6T. Obviously its contribution to the fractional molar volume of the total methylene units will be different; however, the group contribution of a cyclohexyl unit to a polymer molar volume is readily available as given in Table IV.

The application of eq 7 to blends of this amorphous polyamide with the aliphatic polyamides results in the data for χ_{blend} depicted in Figure 9. The experimental confirmation of the phase diagram shown has only been partly investigated. For example, a blend of this amprhous po-

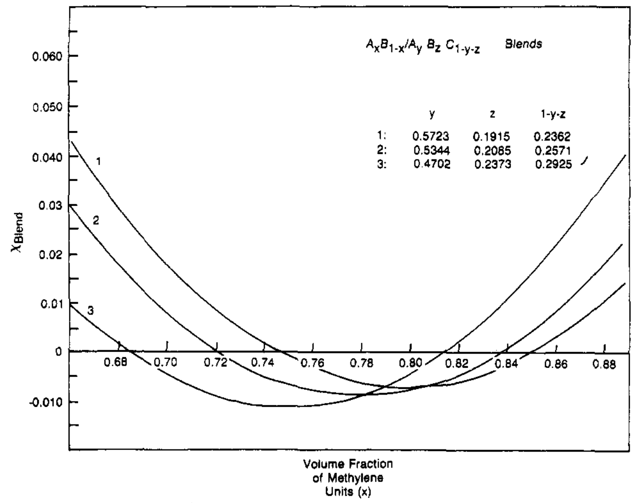


Figure 10. Calculated values of χ_{blend} of blends of $A_xB_{1-x}/A_yB_zC_{1-y-z}$ polyamides: nylon 3Me6T (1); cycloaliphatic polyamide (2); nylon 6IcoT (3).

lyamide containing nylon 12 is known to form an immiscible system.[30] Thus, with a calculated value of $\chi_{\mathrm{blend}} \simeq 0.017$, it is now possible to explain why this occurs. In addition to this, a blend of nylon 66 is predicted to be miscible ($\chi_{\mathrm{blend}} \simeq -0.008$). To support this prediction, blends of nylon 66 and the cycloaliphatic polyamide, produced both by melt- and solution-blending methods, have been shown unequivocally to form a miscible system. A melt-blended nylon 66 composition containing 15% by weight of the amorphous nylon exhibited an increased T_g (56 °C) over that obtained for nylon 66 alone (46 °C). Moreover a solution blend of approximately 50% by weight showed a quench-cooled T_g of approximately 75 °C and an accompanying crystallization exotherm on further heating; a feature not usually visible on heating quench-cooled nylon 66. Experimental evaluation of the phase behavior of this amorphous polyamide in nylon 46, 610, and 612 will provide a rigorous examination of the quantities calculated and the arguments developed thus far. The values of χ_{blend} for these particular systems are quite close to zero and therefore occupy a particularly influential position to test the accuracy of the predictions given in Figure 9.

A composite diagram describing the phase behavior of the three aromatic polyamides, nylon 3Me6T, nylon 6IcoT, and the cycloaliphatic polyamide and their blends of aliphatic polyamides is shown as Figure 10. This illustrates the influence of changes of y on the phase diagram. As y decreases in value, the curve shifts to lower values of x and the width of the window of miscibility increases. The converse is true as y increases. From this type of analysis it should be possible to predict the phase behavior of almost any aromatic polyamide/aliphatic polyamide blend provided it can be rationalized as an $A_xB_{1-x}/A_yB_zC_{1-y-z}$ copolymer blend system.

Aliphatic Polyamide Binary Blends. The bulk of the experimental evidence found in the literature suggests that binary blends of aliphatic polyamides do not form miscible systems.[31-33] It is possible to reconcile these findings with the predictions of the binary interaction model by assuming blends of this type to be a mixture of copolymers, A_xB_{1-x}/A_yB_{1-y}, that differ only in chemical composition. The expression for χ_{blend} for such a system is given as eq 6, where χ_{AB} has been shown to be large and positive ($\chi_{\mathrm{AB}} \simeq 2.685$).

The nature of eq 6 suggests that, at the limit of infinite molecular weights, blends of semicrystalline aliphatic polyamides will always form immiscible systems; i.e., χ_{blend} is always positive. This behavior is illustrated in Figure 11 for blends of aliphatic polyamides containing nylon 6 and nylon 12. Similar curves can be constructed for the other aliphatic polyamides. Within the scheme presented here, nylon 6 and nylon 66 are indistinguishable and should form a miscible blend. Evidence to date is inconclusive; however, there has been a suggestion of partial or limited miscibility.[34]

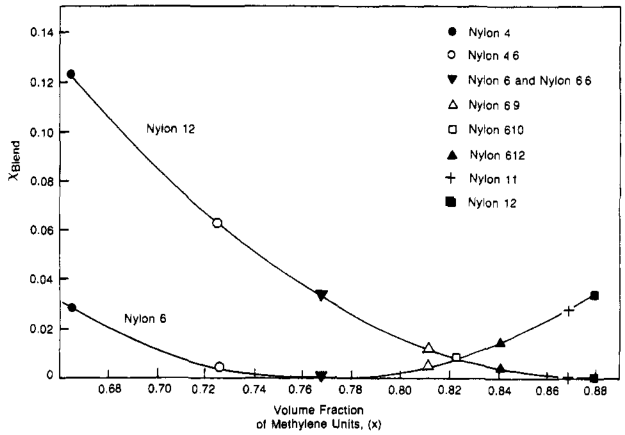


Figure 11. Calculated values of χ_{blend} of blends of aliphatic polyamides, A_xB_{1-x}, containing nylon 6 and nylon 12.

Identical mathematical arguments can also be developed, similar to those above, which can also explain why all aliphatic polyamides will form phase-separated blends with polyolefin polymers, such as polyethylene. In this instance, eq 6 reduces to eq 12, and following from the same reasoning noted previously, χ_{blend} will always be positive; an unfavorable prediction for miscibility.

$$\chi_{\mathrm{blend}} = (1 - y)^2 \chi_{\mathrm{AB}} \tag{12}$$

Aromatic Polyamide Blends. Blends containing only aromatic polyamides can be represented as blends comprised of copolymers with different compositions denoted as $A_yB_zC_{1-y-z}$ and $A_rB_sC_{1-r-s}$. In this instance, it is straightforward to show that the expression for χ_{blend} can be written as eq 13.

$$\begin{aligned}\chi_{\mathrm{blend}} = {} & [y(s - z) + r(z - s)]\chi_{\mathrm{AB}} + \\ & [(1 - y - z)(s - z) + (1 - r - s)(z - s)]\chi_{\mathrm{BC}} + \\ & [(1 - y - z)(r - y) + (1 - r - s)(y - r)]\chi_{\mathrm{AC}}\end{aligned} \tag{13}$$

The application of eq 13 to binary blends of only the aromatic polyamides results in the curves shown in Figure 12. The curves map the phase behavior, in the form of χ_{blend}, of each polyamide blended with a series of polyamides where the variable is r, the volume fraction of methylene units in the blend component $A_rB_sC_{1-r-s}$. From the structure given, the ratio of s to $1 - r - s$ remains essentially constant. The most obvious result is that as in blends containing only semicrystalline polyamides, χ_{blend} is always positive and therefore blends containing only aromatic polyamides should form phase-separated systems.

It is possible to test this prediction by examining the solution behavior of blends of the aromatic polyamides at hand. Equation 13 provides a value of $\chi_{\mathrm{blend}} \simeq 0.006$ for a nylon 3Me6T/nylon 6IcoT blend. Inspection of Figure 13 (curve A) shows a thermogram obtained from a 50:50 blend of these two polymers clearly indicating the presence of two T_g's and the formation of an immiscible system; therefore, a rational physical basis has now been provided as to why these two polymers are both individually miscible with nylon 6 but immiscible with each other. Curves B

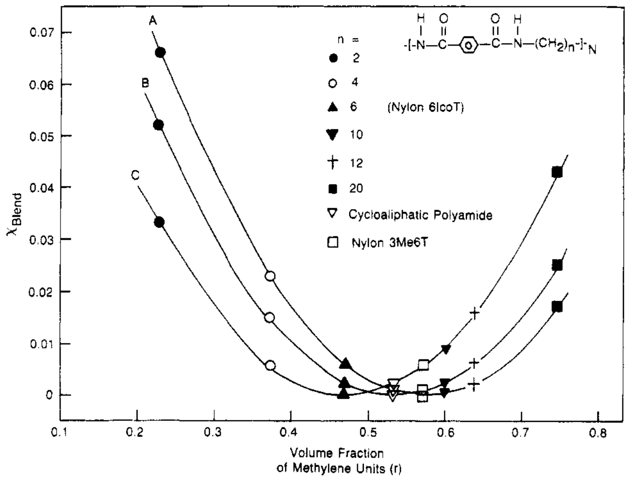


Figure 12. Calculated values of χ_{blend} of $A_yB_zC_{1-y-z}/A_rB_sC_{1-r-s}$ polyamides. Blends are based on nylon 3Me6T (A), cycloaliphatic polyamide (B), and nylon 6IcoT (C).

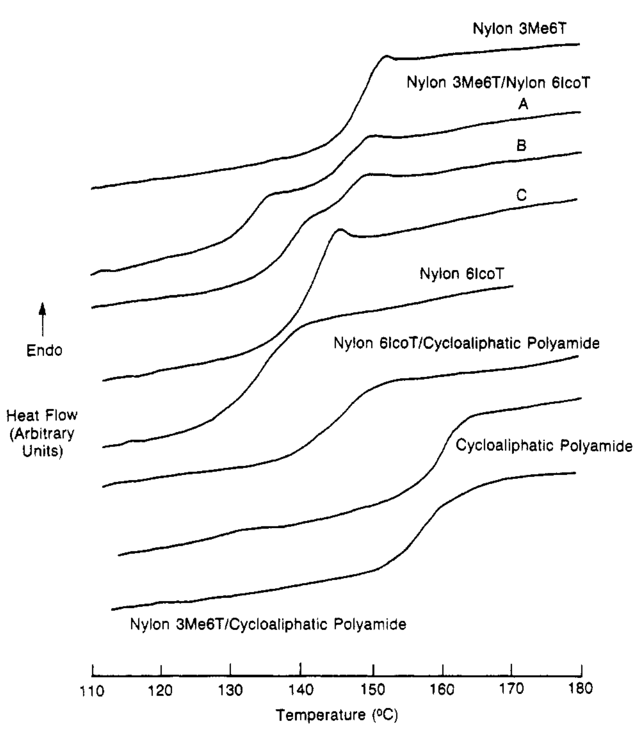


Figure 13. Representative thermograms of amorphous polyamide blends.

and C are thermograms obtained from the same blend exposed to elevated temperature (250 °C) for extended periods of time (B, 1 h; C, 13 h) and illustrate a gradual merging of the two T_g's to form a material with a T_g intermediate between those of the two pure components. Only several minutes at 300 °C produces a thermogram similar to that of curve C. This behavior is highly unlikely to be the result of the presence of an upper critical solution temperature, UCST, but probably exemplifies the effects of transreaction in the melt. The transreaction of these polymers at such a fast rate suggests that the two polymers are only just phase separated and that a broad interface may exist between the two phases. This would result in the close proximity of the two polymer species in order to transreact, a conclusion that can be reconciled with the relatively low value of χ_{blend} ($\simeq 0.006$). The value of χ_{blend} for immiscible polymers has been shown to have an influence on the distribution of polymer species through the interface,[35] such that the thickness of the interface $\sim \chi^{-1/2}$.

Table VIII
Thermal Properties and Phase Behavior of Binary Amorphous Polyamide Blends

blend	T_g of 50:50 blend,[a] °C	obsd blend solution behavior	calcd χ_{blend}[b]
nylon 3Me6T/nylon 6IcoT	128, 144	2 T_g's, immiscible	0.0059
nylon 6IcoT/cycloaliphatic polyamide	139	1 T_g, miscible	0.0023
nylon 3Me6T/cycloaliphatic polyamide	152	1 T_g, miscible	0.0080

[a] Pure component, T_g (°C): nylon 3Me6T, 147; nylon 6IcoT, 127; cycloaliphatic polyamide, 156. [b] Calculated by using eq 13.

Therefore if χ_{blend} is small and positive the interface will be large.

Blends of the cycloaliphatic polyamide with nylon 6IcoT and nylon 3Me6T provided thermograms, also shown in Figure 13, demonstrating the presence of a single T_g intermediate between those of the pure components and thus signifying the formation of miscible blends. Although only a single transition, approximately intermediate between those of the pure components, could be identified for the nylon 3Me6T/cycloaliphatic polyamide blend, the close proximity of the pure component T_g's makes a totally unambiguous conclusion more difficult. It is equally possible that this blend may only be partially miscible. This question could be resolved by the application of aging studies similar to those described recently in the literature.[36]

A summary of the thermal properties and phase behavior of all aromatic polyamide blends is given in Table VIII. At first inspection these results would appear to be at variance with the predictions summarized in Figure 12 and Table VIII, where positive values of χ_{blend} of approximately 0.0008 and 0.0023 were obtained for blends of the cycloaliphatic polyamide with nylon 3Me6T and nylon 6IcoT, respectively. These values of χ_{blend}, although very small, indicate immiscibility. The fact that miscible blends are formed can be explained by considering the influence of the χ_{crit} term, which for these polymers may be significant. Inspection of Table I shows the molecular weight of nylon 6IcoT to be relatively small; consequently a χ_{crit} term $\simeq$ 0.004 would render the blends miscible, as observed. The very small χ_{blend} of 0.0008 for the nylon 3Me6T/cycloaliphatic polyamide blend would also be very susceptible to the influence of the χ_{crit} term and give an overall value for the interaction consistent with the formation of a miscible blend. It is also possible, however, that the overall weight of the simplifications introduced has reached a critical limit and the scheme developed for these polymers is not sufficient to describe their phase behavior with necessary detail. As an addendum to this section, recent studies have shown that nylon 3Me6T is immiscible with a sample of the cycloaliphatic polyamide with a suspected higher molecular weight. This conflicting behavior will form the subject of a further paper.

Miscellaneous Aromatic/Aliphatic Polyamide Blends. The preceding discussion has further verified the ability of the model to account for experimentally observed phase behavior for a number of polyamide systems whose chemical constitutions are extemely diverse. Some examples of blend phase cartography for amorphous/semicrystalline polyamides are presented in Figure 14, which describes the behavior of nylon 6, nylon 610, and nylon 12, respectively, when blended with the various aromatic polyamides as shown. It is apparent from these calculations that nylon 12 is expected to show no tendency to form miscible blends with common aromatic polyamides. On the other hand, nylon 6 can be expected to form miscible blends with aromatic polyamides with a methylene con-

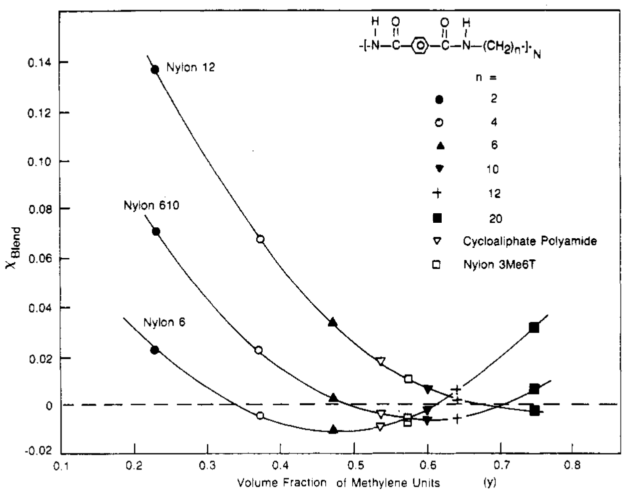
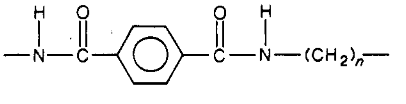


Figure 14. Calculated values of χ_{blend} of some blends of polyamides $A_yB_zC_{1-y-z}$ containing nylon 12, nylon 610, and nylon 6.

tent, or its equivalent, between that of nylon 4T and nylon 10T. There is little or no information in the literature to test these projections. One supporting example, however, is provided by a study of Zimmerman and co-workers.[37] In this study the glass transition behavior and anomalous crystallization behavior of blends of nylon 66 and the monomethylated analogue of nylon 6IcoT, nylon 1Me6T, indicated the formation of a miscible system. Although not recognized at the time, a calculated value of $\chi_{\mathrm{blend}} \simeq -0.01$, when $y = 0.5082$, would certainly substantiate this conclusion.

A crucial feature of the projections described in Figure 14, is the equivalence of methylene interactions in different environments. This becomes particularly critical when considering $A_yB_zC_{1-y-z}$ polymers with small values of y. It is simple to argue that when $n = 6$ or above, for a polymer



the overall methylene interaction is representative of methylene units adjacent to methylene units. However when $n = 2$ or 3 (small y), for example, the methylene interaction should be considered to be more representative of a methylene unit adjacent to an amide unit. The interactions of the methylene units in the two environments cannot automatically be considered to be equivalent. This restrictive condition cannot at present be dealt with quantitatively and as such its possible influence on predicted phase behavior can only be qualitatively recognized. As stated previously, it is possible to circumvent this obstacle to a large extent by the choice of individual mer assignment within the assumed copolymer. However, this in turn imposes restrictions on the segmental interaction parameters calculated and the application of the model to more chemically diverse polymer blend systems. For example, in the less restrictive form described here it is possible to apply the model to blends containing poly(p-terephthalamide) (PPTA, more commonly known as Kevlar).

PPTA molecules are rigid rod structures, which can also be considered to represent the primary member of the homologous series $A_yB_zC_{1-y-z}$, where $y = 0$. Within this framework, values of χ_{blend} for PPTA/aliphatic polyamide blends have been calculated. Blend and copolymer studies involving PPTA structures have suggested thermodynamic miscibility with nylon 6 and nylon 66, respectively.[38,39] This behavior compares favorably with the predicted value of $\chi_{\mathrm{blend}} \simeq -0.046$. Studies involving copolymerization of PPTA and nylon 3 structures,[40] although inconclusive, suggested the opposite, a contradictory outcome when compared to a calculated value of χ_{blend} of approximately -0.035.

The application of the model developed here and the quantities calculated for the various χ_{ij} to blends involving PPTA admittedly represents an extreme test. However, it is worthwhile conducting these calculations, based upon the experimental evidence at hand, provided that it is realized that conclusions with regard to the phase behavior of rigid/flexible molecular polymer blends are difficlut and more complex, not only from a Flory–Huggins point of view but also because of the nature of the rigid rod molecules. PPTA in particular is a wholly crystalline structure with no discernible amorphous regime. This results from a high symmetry of conformation that allows the formation of aggregated ordered units. These features will also be present in any blend, allowing the aggregation of molecules to form an apparent phase-separated system.

Application of the Model to Other Blends. Blends of polyamides and polyesters have been found generally to be immiscible.[41] A brief investigation of a nylon 3Me6T/poly(caprolactone) (PCL) blend, the latter constituting the direct polyester equivalent of nylon 6, has also indicated immiscibility. A blend of nylon 3Me6T and poly(caprolactone) revealed the presence of two T_g's close to those of the pure constituents. An initial response to these observations may include the suggestion of an unfavorable interaction between amide and ester segments. This may indeed be the case; however, the real situation is probably more complex. Within the context of a binary interaction model, the nylon 3Me6T/PCL blend requires six segmental interaction parameters in order to quantify χ_{blend}. The value of the ester/methylene exchange interaction has also been shown to be large and positive,[10] similar to that observed here for the amide/methylene interaction, and therefore it is the overall balance of these interactions which will play a significant role in defining the phase behavior. Thus, the ester/amide exchange interaction may be favorable to mixing but the weight of additional strong unfavorable interactions promotes the immiscible condition. Clearly further studies are required before a less speculative conjecture is possible.

Concluding Comments

The solubility of amorphous aromatic polyamides in aliphatic polyamides has been quantitatively analyzed in terms of a mean-field interaction model. The extension of this simple scheme to polyamide blends in general has confirmed the universal applicability of this type of treatment to complex chemical systems. The critical features of the predictions are contained in the approximations and simplifications introduced in order to apply the model. Accordingly it should be emphasized that these features require further qualification, particularly with regard to the estimation of the upper and lower bound values of the volume fraction of methylene functionalities for the blends containing nylon 3Me6T. A suitable methodology to define these limits with greater accuracy is currently under development and will form the subject of a future paper. Similarly, it should be mentioned that a more accurate evaluation of χ for a suitable aromatic/aliphatic blend would assist in the precise evaluation of the segmental interaction parameters. This could be achieved by a scattering technique or by some other appropriate technique on a blend with an anticipated value of χ which is more negative than that proposed for the nylon 3Me6T/nylon 6 blend.

Registry No. Nylon 4 (SRU), 24938-56-5; nylon 4 (homopolymer), 24968-97-6; nylon 46 (SRU), 50327-22-5; nylon 46 (copolymer), 50327-77-0; nylon 6, 25038-54-4; nylon 66, 32131-17-2; nylon 69 (SRU), 28757-63-3; nylon 69 (copolymer), 27136-65-8; nylon 610 (SRU), 9008-66-6; nylon 610 (copolymer), 9011-52-3; nylon 612 (SRU), 24936-74-1; nylon 612 (copolymer), 26098-55-5; nylon 11 (SRU), 25035-04-5; nylon 11 (homopolymer), 25587-80-8; nylon 12 (SRU), 24937-16-4; nylon 12 (homopolymer), 25038-74-8; nylon 3Me6T (SRU), 9071-17-4; nylon 3Me6T (copolymer), 25497-66-9; nylon 6ICOT (SRU), 58814-83-8; nylon 6ICOT (copolymer), 25750-23-6; Bexloy APC-803, 112721-08-1.

References and Notes

(1) Paul, D. R.; Newman, S. *Polymer Blends*; Academic: New York, 1978.
(2) Olabisi, O.; Robeson, L. M.; Shaw, M. T. *Polymer–Polymer Miscibility*; Academic: New York, 1979.
(3) Barlow, J. W.; Paul, D. R. *Polym. Eng. Sci.* **1987**, *27*, 1482.
(4) Kambour, R. P.; Bendler, J. T.; Bopp, R. C. *Macromolecules* **1983**, *16*, 753.
(5) ten Brinke, G.; Karasz, F. E.; MacKnight, W. J. *Macromolecules* **1983**, *16*, 1827.
(6) Paul, D. R.; Barlow, J. W. *Polymer* **1984**, *25*, 487.
(7) ten Brinke, G.; Rubinstein, E.; Karasz, F. E.; MacKnight, W. J.; Vukovic, R. *J. Appl. Phys.* **1984**, *56*, 2440.
(8) Pfennig, J.-L. G.; Heskkula, H.; Barlow, J. W.; Paul, D. R. *Macromolecules* **1985**, *18*, 1937.
(9) Udea, H.; Karasz, F. E. *Macromolecules* **1985**, *18*, 2719.
(10) Woo, E. M.; Barlow, J. W.; Paul, D. R. *Polymer* **1985**, *26*, 763.
(11) Min, K. E.; Chiou, J. S.; Barlow, J. W.; Paul, D. R. *Polymer* **1987**, *28*, 1721.
(12) Fowler, M. E.; Barlow, J. W.; Paul, D. R. *Polymer* **1987**, *28*, 1177.
(13) O'Gara, J. F.; Williams, D. J.; MacKnight, W. J.; Karasz, F. E. *J. Polym. Sci. Polym. Phys. Ed.* **1987**, *25*, 1519.
(14) Min, K. E.; Paul, D. R. *Macromolecules* **1987**, *20*, 2828.
(15) Ellis, T. S. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1987**, *28*, 181.
(16) Ellis, T. S. *Polymer*, in press.
(17) Howe, S. E.; Coleman, M. M. *Macromolecules* **1986**, *19*, 72.
(18) Painter, P. C.; Park, Y.; Coleman, M. M. *Macromolecules* **1988**, *21*, 66.
(19) Scott, R. L. *J. Chem. Phys.* **1949**, *17*, 279.
(20) Balazs, A. C.; Karasz, F. E.; MacKnight, W. J.; Ueda, H.; Sanchez, I. C. *Macromolecules* **1985**, *18*, 2784.
(21) Schulz, O.; Cantow, H. J. *Polym. Bull.* **1986**, *15*, 449.
(22) Epstein, B. N.; Latham, R. A.; Dunphy, J. F.; Pagilagan, R. U. *Advances in Toughened Nylon*; 130th Meeting of the Rubber Division, American Chemical Society, Atlanta, GA, 1986; Paper 26.
(23) Van Krevelen, D. W. *Properties of Polymers*; Elsevier: New York, 1976.
(24) Kotliar, A. M. Macromol. Rev. **1981**, *16*, 367.
(25) Kakar, S. K. *Textile Res. J.* **1976**, *46*, 776.
(26) Nishi, T.; Wang, T. T. *Macromolecules* **1975**, *8*, 909.
(27) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953.
(28) Hoffman, J. D.; Weeks, J. J. *J. Chem. Phys.* **1962**, *37*, 1723.
(29) Wunderlich, B. *Macromolecular Physics*; Academic: New York, 1980; Vol. 3.
(30) Ellis, T. S. *J. Appl. Polym. Sci.* **1988**, *36*, 451.
(31) Kitao, T.; Kobayashi, H.; Ikegami, S.; Ohya, S. *J. Polym. Sci., Polym. Chem. Ed.* **1973**, *11*, 2633.
(32) Ong, E. S.; Kim, Y.; Laverne-Williams, H. *J. Appl. Polym. Sci.* **1986**, *31*, 367.
(33) Kyotani, M. *J. Macromol. Sci., Phys.* **1982**, *B21*, 219.
(34) Verma, A.; Deopura, B. L.; Sengupta, A. K. *J. Appl. Polym. Sci.* **1986**, *31*, 747.
(35) Helfand, E.; Tagami Y. *J. Chem. Phys.* **1971**, *56*, 3592.
(36) Bosma, M.; ten Brinke, G.; Ellis, T. S. *Macromolecules* **1988**, *21*, 1465.
(37) Zimmerman, J.; Pearce, E. M.; Miller, I. K.; Muzzio, J. A.; Epstein, I. G.; Hosegood, E. A. *J. Appl. Polym. Sci.* **1973**, *17*, 849.
(38) Takayanagi, M.; Ogata, T. *J. Macromol. Sci., Phys.* **1980**, *B17*, 591.
(39) Kanakalatha, P.; Vijayan, K.; Sridhar, M. K.; Singh, A. K. *Polymer* **1983**, *24*, 621.
(40) Moore, D. R.; Mathias, L. J. *J. Appl. Polym. Sci.* **1986**, *32*, 6299.
(41) Pillon, L. Z.; Utracki, L. A. *Polym. Eng. Sci.* **1984**, *24*, 1300.

Solution Properties of Ionomers. 2. Simple Salt Effect

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ABSTRACT: The effect of simple salts on the solution properties of sulfonated polystyrene ionomers was studied by viscosity and light scattering measurements. It was shown that the polyelectrolyte behavior of ionomers in a polar solvent was suppressed by the addition of simple salts (LiCl). A single peak in the reduced viscosity vs concentration curve was observed when salt concentration was 1×10^{-4} M. It was found that the addition of simple salts also suppressed the aggregation behavior of ionomers in a low-polarity solvent. However, the addition of excess neutralizing agent (LiOH) seemed to enhance the aggregation at high concentration.

Introduction

Ion-containing polymers, such as polyelectrolytes, biopolymers, glasses, etc., have attracted the attention of researchers for many years.[1-5] The most recent addition to these ion-containing polymers is ionomers which have a small number of ionic groups (i.e., up to 10–15 mol %) along a nonionic backbone chain.[6-8] Because of their special properties, such as excellent mechanical properties, high transparency, and oil resistance, ionomers have mostly been utilized and studied in the solid state. It is now well recognized that the large change in properties of ionomers is due to the clustering of ion pairs in nonionic medium of low dielectric constant.

In contrast to the study of ionomers in the solid state, little work has been done on the solution properties of ionomers. However, during the past several years, the study of solution properties has become active and interesting results have been reported.[9-24] It has now been well established that ionomers show two types of behavior according to the polarity of solvents:[11,23] (1) polyelectrolyte behavior due to electrostatic interactions between ionic groups and small ions in polar solvents; (2) aggregation behavior due to the attraction of ion pairs in low-polarity or nonpolar solvents.

There are many molecular parameters that may influence the solution properties of ionomers. These are molecular weight, ion content, counterion, ion distribution, degree of neutralization, and the presence of simple salts. A systematic study on the effect of ion content was previously reported;[11] the higher the ion content, the larger