Aromatic Polyamide Blends: Enthalpy Relaxation and Its Correlation with Phase Phenomena

Thomas S. Ellis

Polymers Department, General Motors Research Laboratories, Warren, Michigan 48090.

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ABSTRACT: The phase behavior of blends containing only aromatic polyamides has been investigated, and the results compared with a predictive treatment founded upon a mean-field binary interaction model. The similarity of structure and composition of the polymers, and hence the close proximity of the respective glass transition temperatures, necessitated the implementation of the technique established by Ellis and ten Brinke to evaluate phase phenomena within the blends. Relying on the structural dependence of the kinetics of enthalpy recovery, this technique has proven to be very sensitive and provides information that is available by no other technique. The prediction of immiscibility was found to be supported in most cases and confirms the axiom that polymers of similar constitution will not form homogeneous mixtures. Noted exceptions to this rule were also found, suggesting that there exists the potential for subtle behavior that is not yet accounted for. The elements possibly contributing to this are addressed and discussed in terms of the applicability of a binary interaction model to blends of this nature.

Introduction

It is now clearly evident[1,2] that an analysis based upon the structural dependence of the kinetics of enthalpy recovery in polymer blends is a sensitive method of establishing phase phenomena in systems normally considered to be immune to the usual thermoanalytical techniques. Consequently, this form of analysis should prove to have an applicability to many different blend systems. While the results presented here are intended to confirm and extend the efficacy of these procedures, the purpose of this communication is 2-fold. In addition to demonstrating the utility of enthalpy relaxation to determine phase behavior in blends whose constituent polymers have virtually coincident glass transition temperatures, T_g, it is also intended to examine the ability of a predictive treatment to describe the phase behavior of binary aromatic polyamide blends.

Recent communications[3-5] have devised a detailed framework from which to investigate the structural factors controlling phase behavior in polyamide–polyamide blends. This has been achieved by treating polyamides as copolymers, composed of elementary chemical functionalities, and the application of a mean-field binary interaction model.[6-8] A component of these discussions involved the question of (im)miscibility in blends containing only aromatic polyamides. The predictive model was very explicit with regard to evaluating phase behavior in these systems; however, there was only a limited quantity of experimental data at hand to compare with the calculated behavior. This subject has now been investigated further involving a number of different aromatic polyamides, and in view of the improved quantitative definition of the model boundaries,[5] a more meaningful examination of this question should now be possible. In a separate, but related issue, the results obtained here may also have a relevance to other blend systems, usually designed to behave as molecular composites, and involving rigid-rod aromatic polyamides. Continued interest in this subject has grown into studies involving binary blends of polyamides[9,10] which have included purely aromatic polyamides.[9] It is of interest to note that the implementation of arguments presented in this communication indicates that there should be a favorable interaction between the various polyamides in these blends. Although blends of this nature may well prove to be beyond the scope of the work presented here, the prizes that may be obtained justify the extension of calculations to these systems.

Experimental Section

Materials. Many of the polymers utilized in this study have been described previously;[3,5] however, a brief summary will also be included here, as shown in Tables I and II. The nylon 3Me6T (Trogamid T obtained from Dynamit Nobel) contains only the terephthalic acid whereas the nylon 6IcoT (Zytel 330, Du Pont) and nylon 6IcoTA (Bexloy AP C-803, Du Pont) both contain a mixture of isophthalic and terephthalic acids in the approximate ratio of 2:1. The nylon 6IcoTA also contains a mixture of diamines, as noted in Table I, resulting in a random copolymer of the species shown. The nylon 12IA (Grilamid TR 55, Emser Industries) is a random copolymer of isophthalic acid (P), 12-aminododecanoic acid (L), and bis(4-amino-3-methylcyclohexyl)methane (B) in the proportions noted in Table I. The composition of this material was determined by NMR in a similar manner to all the nylons mentioned previously. In addition to this, a diad sequence analysis of the nylon 12IA has indicated that the relative proportion of the various sequences are LL = 12%, PL = 23%, PB = 42%, and LB = 23%.

Procedures. All blends (50:50 w/w) were prepared by coprecipitation into diethyl ether from a common solvent based on trifluoroethanol and methylene chloride (3:2 v/v). The filtered precipitates were washed extensively and dried in a vacuum oven at ambient (16 h) and then at 80 °C (8 h). In order to assure sampling uniformity, the pure polymers were subjected to an identical preparative procedure.

The molecular weight characteristics of the polymers were determined by size exclusion chromatography (GPC) in a solution of *m*-cresol at 110 °C. Molecular weight averages were computed on the basis of a universal calibration provided by polystyrene standards.

Thermal Analysis. Unless stated otherwise, thermal analysis was conducted at a heating rate of 20 °C/min by using a Perkin-Elmer Series 7 differential scanning calorimeter (DSC) calibrated for temperature and enthalpy using indium. Measurements of T_g are reported as the onset value. Characterization of phase behavior was effected by using the technique relying on enthalpy recovery similar to that described in more detail in the literature.[1,2] For this type of analysis, measurements of the onset, T_{ons}, and maximum, T_{max}, of the enthalpy recovery peak are identical with those defined previously.[11] Measurements of the enthalpy difference, ΔH_D, resulting from annealing, were made on the subtracted thermogram of an aged and quench-cooled sample following the recommendations of Richardson and Savill.[12] Figure 1 provides a schematic summary

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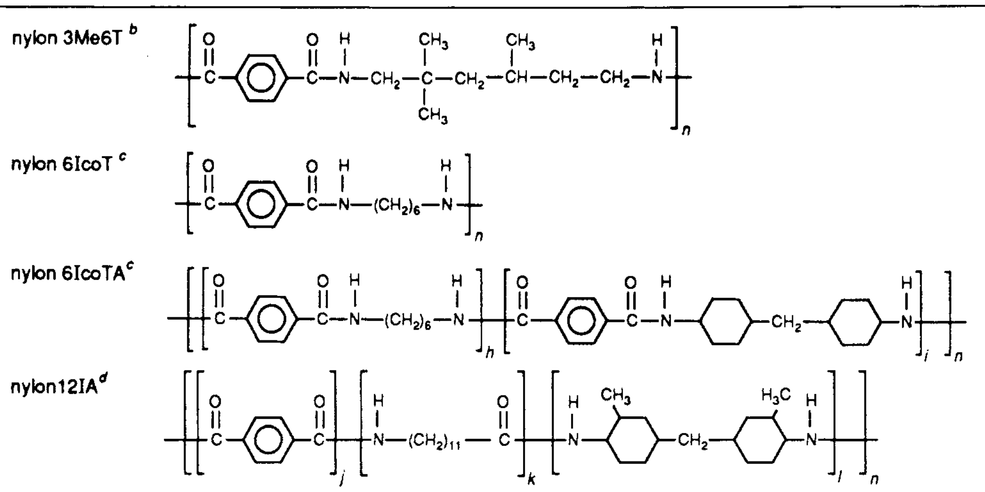
Table I
Chemical Structure of the Aromatic Polyamides[a]



[a] h:i is approximately 0.69:0.31 in a random copolymer. j:k:l is approximately 1:1:1 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.

Table II
Properties and Characteristics of the Aromatic Polyamides

				mer volume fractn[b]		
	T_g,[a] °C	$10^{-3}M_n$	$10^{-3}M_w$	methylene y	amide z	phenyl $1 - y - z$
nylon 3Me6T	151.0	20.0	63.0	0.5723	0.1915	0.2362
nylon 6IcoT	129.0	14.1	49.8	0.4702	0.2373	0.2925
nylon 6IcoTA	163.4 (160.7)	18.0	45.0	0.5344	0.2085	0.2571
nylon 12IA	158.0	29.5	62.5	0.7514	0.1376	0.1110

[a] Measured at 20 °C/min. [b] Calculated by using group contribution to molar volume of polymers.[25]

of the treatment of a thermogram showing the characteristic enthalpy recovery and the determination of the parameters defined above. The annealing temperature, T_a, unless stated otherwise, was 143.0 °C after first exposing the blend to 190 °C for 10 min. The thermogram from an aged sample was recorded after annealing for a given time, t_a, and subsequent cooling to 80 °C. An additional parameter denoted as h_r (W/g), the height of the recovery peak (see Figure 1), was also measured for a number of the blends.

Theoretical Background

Previous communications[3,5] have laid a foundation from which to project the phase behavior of nylon blends, irrespective of their composition, provided that the polymer structure can be rationalized in terms of methylene, amide, and phenyl functionalities. This particular form of *mer* unit subdivision was chosen because it represented the least restrictive nomenclature. While it is not intended to provide a detailed discussion here of all the features surrounding the application of the model, it should be emphasized that the sequence order of *mer* unit and their spatial arrangement may well exercise a profound influence on phase behavior. Notwithstanding these important questions, this formalism has shown great success with respect to predicting the phase behavior of aliphatic/aromatic polyamide blends. In contrast, only a limited amount of information has been available to examine the ability of this predictive model to describe the behavior of binary aromatic polyamide blends. In view of the chemical complexity of the polymers, described previously, the studies undertaken here will provide a rigorous examination of the ability of the model to account for diverse polymer systems.

By expressing the mixing free energy balance in the convenient form of Flory–Huggins lattice theory, eq 1 emphasizes the role of the interactional term χ_{12}, as a determinant of phase behavior in high molecular weight polymer blends.

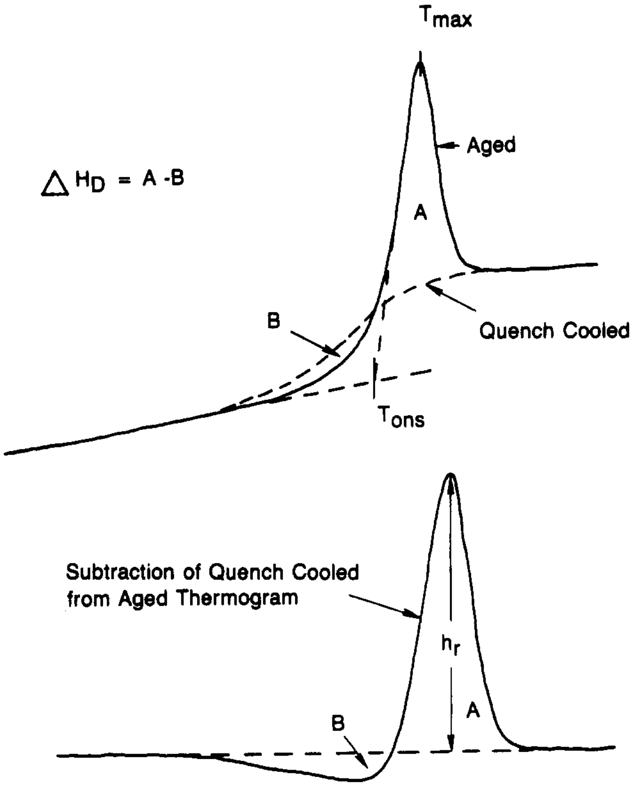


Figure 1. Schematic illustration of thermograms obtained from aged and quench-cooled samples indicating the measured parameters T_{ons}, T_{max}, ΔH_D, and h_r.

$$\frac{\Delta G_m}{RT} = \left[\frac{1}{N_1}(\phi_1 \ln \phi_1) + \frac{1}{N_2}(\phi_2 \ln \phi_2)\right] + \chi_{12}\phi_1\phi_2 \quad (1)$$

Thus as a first approximation, for miscibility to occur, the mandatory negative ΔG_m is usually provided by $\chi_{12} < 0$. The first two terms of eq 1, where N is the degree of polymerization and ϕ is the volume fraction, represent the combinational entropy of mixing. A number of workers[13,14] have highlighted the need to express eq 1 on a unit volume basis owing to the nonequivalence of monomer unit volume. However, for the purpose of discussion, this is not necessary here. For a mixture of random copolymers it has been proposed[4-8] that χ_{12} can be written in terms of segmental interaction parameters, χ_{ij}, given by eq 2. The χ_{crit} term has its usual meaning

$$\chi_{12} \equiv \chi_{blend} = f[\chi_{ij}] - \chi_{crit} \quad (2)$$

as shown in eq 3 such that the above expression reduces to eq 4 in the limit of infinite molecular weights. In this

$$\chi_{crit} = (N_1^{-1/2} + N_2^{-1/2})^2/2 \quad (3)$$

$$\chi_{blend} = f[\chi_{ij}] \quad (4)$$

format χ_{blend} is an effective interaction parameter indicating miscibility ($\chi_{blend} < 0$) and immiscibility ($\chi_{blend} > 0$).

Alternative descriptions of Flory–Huggins lattice theory are available[15,16] to account for blends containing strongly interacting units, e.g., hydrogen bonding. This approach equates the enthalpic contribution to the free energy of mixing with a dispersive term and a chemical equilibrium term arising from hydrogen-bonding interactions. For binary polyamide blends, however, it has been proposed[3-5] that the repulsive interactions dominate the phase behavior even though inter- and intrahydrogen-bonding interactions exist in the pure polymers and the blends. A corollary of this reasoning states that the net change of hydrogen bonding within the blend is essentially zero.

Blends of aromatic polyamides can in general be represented as $A_yB_zC_{1-y-z}/A_rB_sC_{1-r-s}$ copolymer blends where the effective interaction parameter, χ_{blend}, can be calculated according to eq 5.[3,4]

$$\begin{aligned}\chi_{blend} = {} & [y(s-z) + r(z-s)]\chi_{AB} \\ & + [1 - y - z(s-z) + (1-r-s)(z-s)]\chi_{BC} \\ & + [1 - y - z(r-y) + (1-r-s)(y-r)]\chi_{AC} \quad (5)\end{aligned}$$

A, *B*, and *C* represent methylene, amide, and phenyl units, respectively, the subscripts are the respective *mer* volume fractions, and the various χ_{ij} represent the segmental interaction parameters, where $\chi_{AB} = 7.982$, $\chi_{BC} = 7.46$, and $\chi_{AC} = -0.288$.[5] Model calculations have shown that χ_{blend}, an indicator of phase behavior, will generally be positive for blends containing polymers of the composition given in Table I and therefore favorable for immiscibility, i.e., the formation of a phase-separated system. It is interesting to note, however, that nylon 12IA is predicted to have negative values of χ_{blend} in a particular but small range of composition. This exception arises because of a small quantity of additional amide units, not adjacent to phenyl groups, introduced by poly(laurolactam) sequences. A pictorial summary of these calculations is shown in Figure 2 for blends of the aromatic polyamides described previously, when blended with a homologous series of aromatic polyamides. As can be seen, the results imply a rather negative projection with respect to the ability of the model to predict phase behavior within this category of blends since the polymer blends in general are always expected to be immiscible. However, it has been noted previously[4] that a blend of nylon 6IcoT is miscible with nylon 6IcoTA, demonstrating that the real situation is not as simple as that described by the model thus far. Some of the possible reasons for this observation will be discussed here.

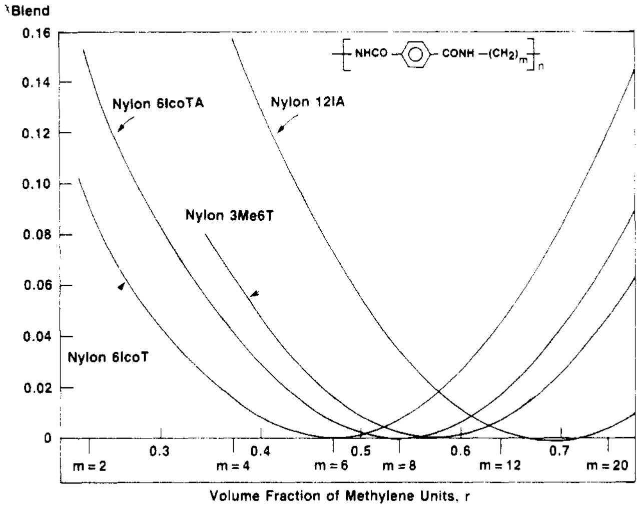


Figure 2. Calculated values of χ_{blend} for aromatic polyamides nylon 3Me6T, nylon 6IcoT, nylon 6IcoTA, and nylon 12IA in a homologous series of aromatic polyamides. Obtained by using eq 5.

Results and Discussion

1. Experimental Verification of Blend Phase Behavior. Blends Containing Nylon 6IcoT. Nylon 6IcoT has a T_g that is substantially different from the other polyamides (see Table II); consequently, it is straightforward to employ the criterion of a single composition sensitive T_g in a miscible blend as an indicator of phase behavior. A blend of nylon 6IcoT and nylon 3Me6T has been shown to be completely immiscible,[4] and measured values of T_g for the two different phases of 131 and 148 °C (cf. 129 and 151 °C for the pure polymers) support this conclusion. A thermogram illustrating the behavior described above is also shown in Figure 3 (thermogram A). In contrast, nylon 6IcoT has been shown to form a completely miscible blend with nylon 6IcoTA.[4] The thermograms B (nylon 6IcoTA) and C (the blend) shown in Figure 3 demonstrate the substantial shift of T_g for the blend compared to that obtained from pure nylon 6IcoTA. Using measured values of the incremental change of heat capacity at T_g for nylon 6IcoTA and nylon 6IcoT of 0.39 and 0.36 J/g K, respectively, theory[17] predicts that a 50:50 blend should possess a T_g of approximately 145 °C. A measured value of 143 °C would appear to substantiate complete miscibility.

Also shown in Figure 3 is the thermogram (F) obtained from a blend of nylon 6IcoT and nylon 12IA and as can be seen again there is little difficulty in the detection of immiscibility between these two polymers. The T_g's of the two phases were measured as 131 and 155 °C, respectively (cf. 129 and 157 °C for the pure polymers).

Blends Containing Nylon 3Me6T. The evaluation of the phase behavior of blends of nylon 3Me6T containing nylon 6IcoTA and nylon 12IA, respectively, was complicated by the close proximity of the respective T_g's of the materials involved. It had been noted in a previous study[4] that on the evidence available nylon 3Me6T appeared to be miscible with nylon 6IcoTA. In that par-

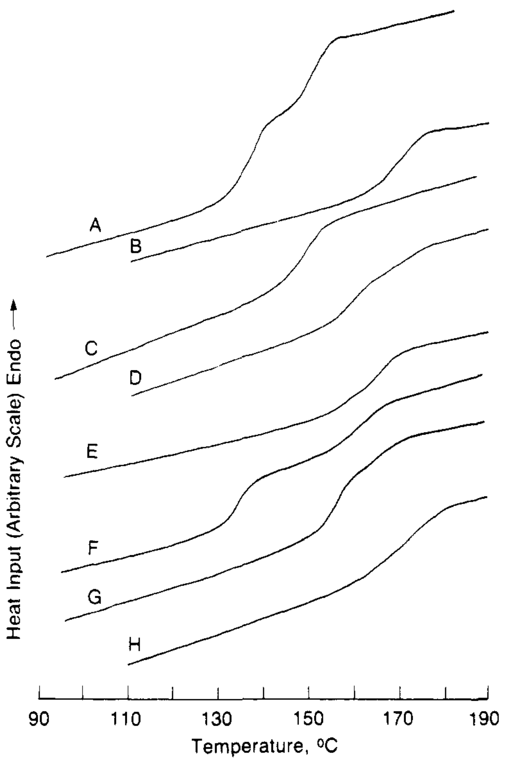


Figure 3. Representative thermograms of aromatic polyamides and their blends, quench-cooled from 190 °C: A, nylon 3Me6T/nylon 6IcoT; B, nylon 6IcoTA; C, nylon 6IcoTA/nylon 6IcoT; D, nylon 6IcoTA/nylon 3Me6T; E, nylon 12IA; F, nylon 12IA/nylon 6IcoT; G, nylon 12IA/nylon 3Me6T; H, nylon 12IA/nylon 6IcoTA.

ticular instance the T_g of the blend (152 °C) was approximately intermediate between values obtained for the pure polymers (147, 156 °C; 10 °C/min heating rate). As part of a detailed study of the phase behavior of these blends, more rigorous calorimetric studies were undertaken to provide definitive information. The details of this new technique are now well documented in the literature;[1,2] however, a brief review will also be given here.

Until recently, it has generally been believed[18,19] that thermoanalytical techniques, e.g., DSC, could not be used to examine phase behavior in polymer blends whose constituent polymers had T_g's in close proximity to each other (10–20 °C apart). By relying on the phenomenon of physical aging[20] and the inherent structural dependence of the kinetics[21] of physical aging in the form of enthalpy recovery, it has been shown that this phenomenon is a sensitive indicator for probing phase behavior in blends.[1,2] Upon annealing a polymer, at a temperature, T_a, below its T_g, there is a decrease of enthalpy which is recovered on heating through T_g providing a thermogram as shown in Figure 1. The characteristic features defining the position of the specific heat overshoot, T_{max} and T_{ons}, are linear with the logarithm of the aging time, t_a.[11,21] In a phase separated blend it is possible to generate two aging peaks whose aging kinetics will approximate those of the pure polymers. A miscible blend, in contrast, will generate a single peak indicating aging kinetics intermediate between those of the pure polymers.[1,2]

A summary of the aging characteristics of nylon 3Me6T, nylon 6IcoTA, and a blend that has been judged to be miscible is shown in Figures 4 and 5. The thermograms obtained from nylon 3Me6T in Figure 4 illustrate qualitatively a rapid approach to thermodynamic equilibrium at the aging temperature of 143 °C. Quantitative evidence to this effect is also shown in Figures 5 and 6 where T_{max}, T_{ons}, and the enthalpy difference ΔH_D between the aged and quench-cooled states are shown to stabilize at higher values of log t_a. The nylon 6IcoTA does not attain equilibrium during the time scale of the investigation and develops a considerable specific heat overshoot on aging for a long time, as shown in Figure 4. As expected T_{max}, T_{ons}, and ΔH_D are linear functions of log t_a and are also shown in Figures 5 and 6. The blend of these two materials displays an aging endotherm intermediate between that of the two pure polymers. This is evident in all respects, as shown in Figures 4 and 5, and is clearly indicative of homogeneous behavior consistent with the formation of a completely miscible blend. The quantities T_{max} and T_{ons} are also linear functions of log

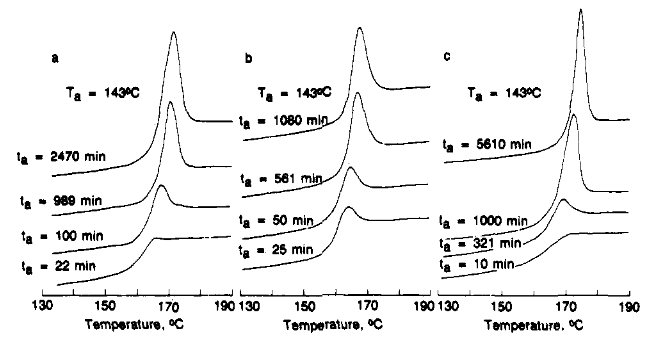


Figure 4. Representative thermograms of nylon 3Me6T (a), nylon 6IcoTA (c), and their blend (b).

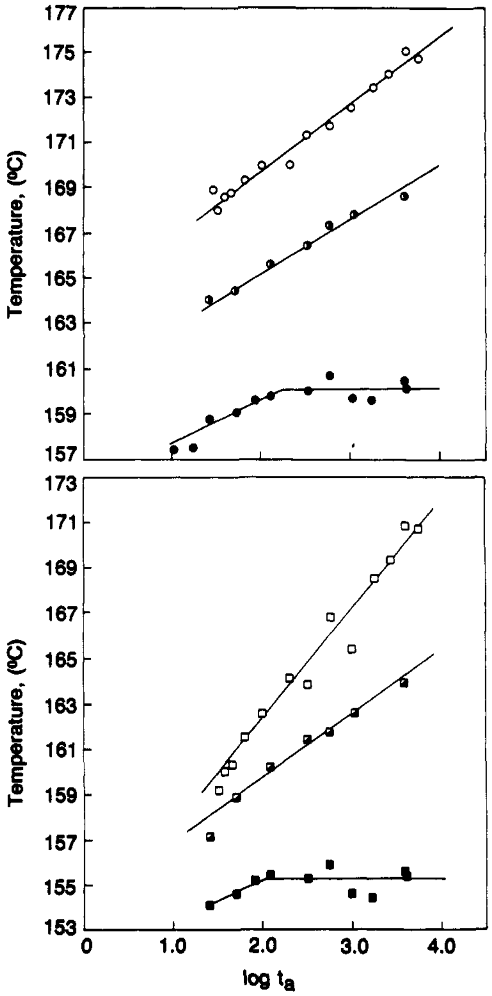


Figure 5. Aging kinetics of nylon 6IcoTA (T_g = 160.7 °C)/nylon 3Me6T blend: ○, ◐, and ●, T_{max} of nylon 6IcoTA, blend (one recovery peak as shown in Figure 4), and nylon 3Me6T, respectively; □, ◪, and ■, T_{ons} of nylon 6IcoTA, blend, and nylon 3Me6T, respectively.

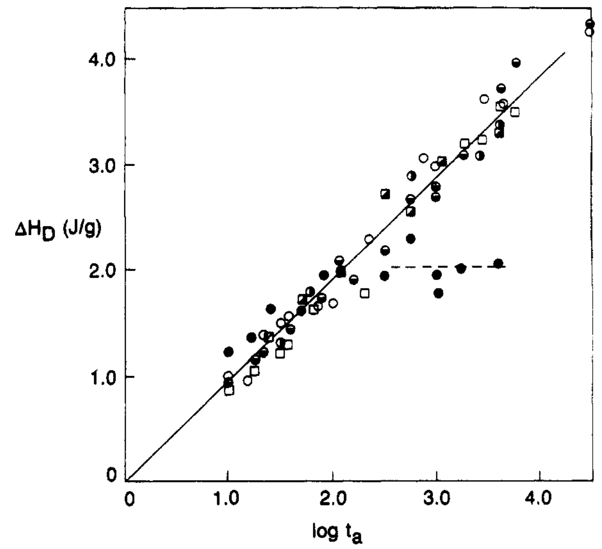


Figure 6. Enthalpy difference between aged and quench cooled thermograms: ●, nylon 3Me6T; □, nylon 6IcoTA; ○, nylon 12IA; ◪, nylon 3Me6T/nylon 6IcoTA; ◑, nylon 12IA/nylon 3Me6T; ◓, nylon 12IA/nylon 6IcoTA.

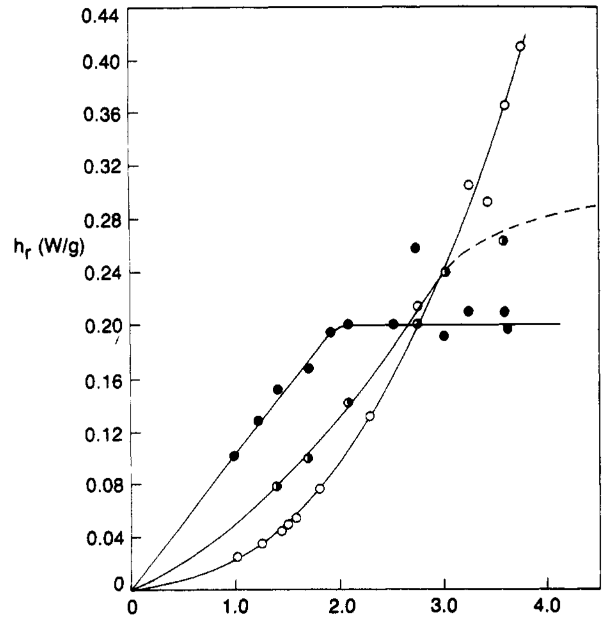


Figure 7. Recovery peak height of nylon 3Me6T (●), nylon 6IcoTA (T_g = 160.7 °C) (○), and their blend (50:50) (◑).

t_a, and the position of the recovery peak appears to be approximately between that of the two polymers. It is important to note, however, that the enthalpy difference, shown in Figure 6 remains essentially constant.

Initial considerations[1] had also suggested that measurements of ΔH_D may prove to be an additional parameter with which to investigate polymer miscibility in blends such as these. While this may still be true for certain special cases, Figure 6 shows this not to be applicable for the blends investigated here. The insensitivity of ΔH_D in all the pure polymers and the blends, shown in Figure 6, is probably related to the similarity of structure of the polymers. Perhaps a more useful parameter to probe blend phase behavior is the height of the recovery peak, h_r, as defined in Figure 1. Application of this measurement to the nylon 3Me6T/nylon 6IcoTA blend results in the data shown in Figure 7. Again the behavior of the blend is seen to be approximately a linear average between that observed for the two pure materials, even through the threshold where the nylon 3Me6T attains thermodynamic equilibrium.

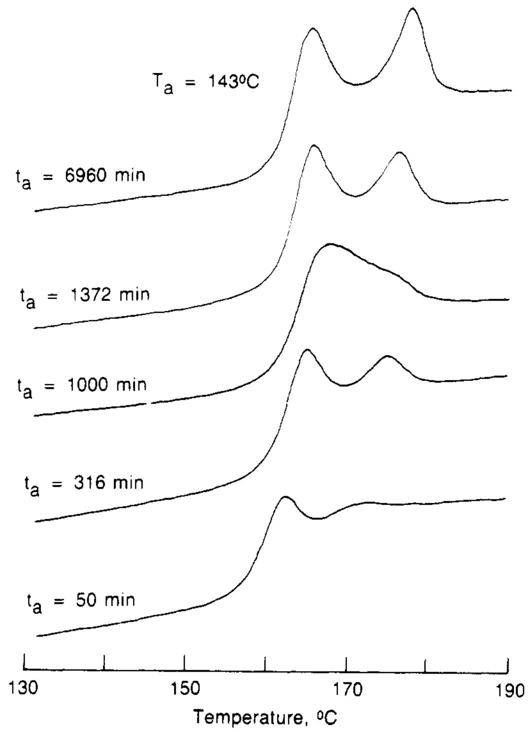


Figure 8. Representative thermograms of nylon 3Me6T/nylon 6IcoTA (T_g = 163.4 °C) blend.

The foregoing results and discussion are clearly consistent with previous observations,[4] which lead to a conclusion of miscibility; however, a blend of nylon 3Me6T with a different source sample of nylon 6IcoTA has yielded different and conflicting behavior. Although the reasons for this different behavior will be advanced shortly, it is believed that purely conformational reasons underly the phenomenon. The influence of this structural variable on polymer blend phase behavior has only a few examples to illustrate its importance; therefore a detailed analysis of this phenomenon will be given.

The occurrence of different phase behavior in blends of nylon 3Me6T and nylon 6IcoTA was noted briefly in an earlier communication[4] and, although was discovered quite fortuitously, was thought originally to be related to differences of molecular weight of the nylon 6IcoTA. No significant differences of molecular weight between the two samples were found. The thermogram D, shown in Figure 3, illustrates a quench cooled thermogram from this blend which, although poorly defined, displays apparent heterogeneity. Aging studies, illustrated by the thermograms reproduced in Figure 8 showing two peaks, confirm the presence of a two phase structure and contrasts quite markedly to the thermograms shown in Figure 4. An examination of the quantitative aspects (T_{max}) of the aging studies, as shown in Figure 9, confirms the presence of an almost pure nylon 6IcoTA phase and a nylon 3Me6T rich phase containing some nylon 6IcoTA. This latter phase shows a measurable shift (3–4 °C) of T_{max} and T_{ons} to a higher temperature but still appears to attain thermodynamic equilibrium upon annealing at 143 °C as noted by the stabilization of these quantities beyong aging times of 1000 min. In all the blends showing phase separation only the value of T_{ons} for the primary recovery peak can be measured reliably.

It is probable that this particular blend is in a state of incipient phase separation at T_g. The information shown in Figures 8 and 9 was obtained after the blend was exposed

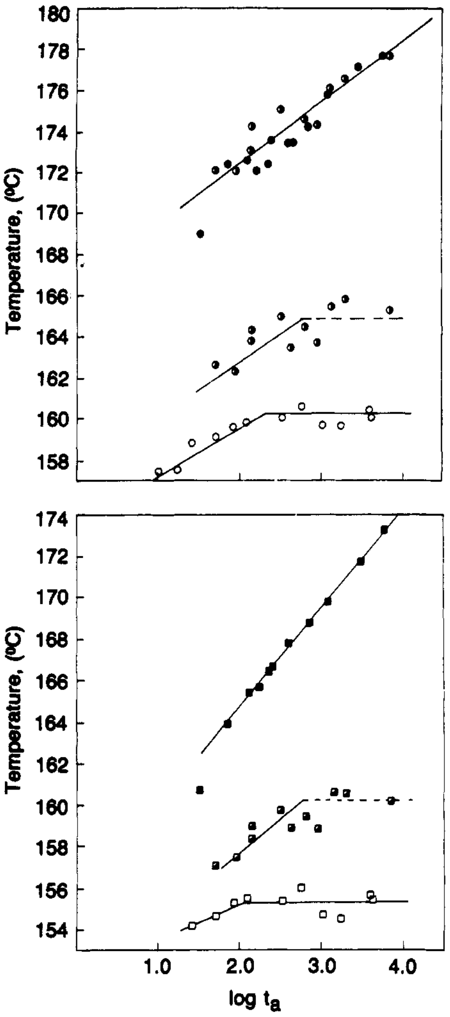


Figure 9. Aging kinetics of nylon 6IcoTA (T_g = 163.4 °C)/nylon 3Me6T blend: ●, ◐, and ○, T_{max} of nylon 6IcoTA, blend (two recovery peaks as shown in Figure 8), and nylon 3Me6T, respectively; ■, ◧, and □, T_{ons} of nylon 6IcoTA, blend, and nylon 3Me6T, respectively.

to 230 °C for 5 min prior to enthalpy recovery measurements. The thermogram shown in Figure 8 (t_a = 1000 min) represents a blend exposed to the standard 190 °C for 10 min and illustrates incomplete phase separation. An identical thermogram is obtained even after exposure to 190 °C for 1 h which suggests that viscosity or time considerations do not arise here and that the blend is only just phase separated under these thermal conditions. Further evidence to support this is shown in the position of T_{max} of the primary recovery peak relative to that obtained when t_a = 1372 min. The T_{max} is at a higher temperature when t_a = 1000 min clearly indicative of a phase much richer in the nylon 6IcoTA than when the blend had been exposed to 230 °C.

The preceding discussion also allows two separate inferences to be made. The first is that the thermal technique described here is very sensitive and provides information which was hitherto generally not available. The second is that despite short exposure to a temperature only approximately 30 °C above the T_g of the blend, compositional equilibrium is attained very quickly.

Reasons for the occurrence of two different species of nylon 6IcoTA are not completely resolved, and it should be emphasized that the polymers used here are of commercial origin beyond the control of this study. Despite careful thermal, NMR, and chromatographic analyses of both samples, the only significant and irrefutable difference between the two samples is that the material forming the immiscible blend with nylon 3Me6T has a higher T_g (163.4 °C) compared to the original source (T_g = 160.7 °C). This slight change of thermal property also results in a comparable shift of aging kinetics to a higher temperature and could possibly be the result of slight compositional variations emanating from the relative proportions of 1,3- and 1,4-benzenedicarboxylic acids or the relative proportions of 1,6-hexanediamine and bis(4-aminocyclohexyl)methane used in the polymerization.[22] No significant differences in composition between the two polymers could be detected by NMR; however, this does not preclude the existence of a slight compositional variation beyond the limits of quantitative detection. Previous studies[23] have also shown that the isomeric composition of the alicyclic derivative can have a substantial influence upon T_g of various polyamides even though the compositional constitution of the polymer remains unchanged. Essentially, this constituent can exist in a number of different conformations within the polymer and a modest variation of this structural element could produce changes of T_g of the order noted ($\simeq$2–3 °C). To confirm this supposition, ^{13}C NMR of the two forms of nylon 6IcoTA has revealed slight quantitative differences related to the carbons of the alicyclic derivative that have been attributed to differences of isomeric composition used for the two polymers. Reasons for the ability of this apparently subtle change of polymer structure to influence phase behavior will be discussed in a later section.

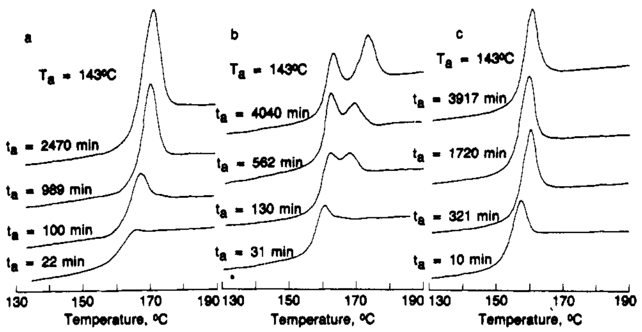


Figure 10. Representative thermograms of nylon 3Me6T (a), nylon 12IA (c), and their blend (b).

The blend of nylon 3Me6T and nylon 12IA was also found to have a quench cooled T_g (thermogram G in Figure 3) which did not allow any conclusion to be made with regard to phase behavior. Enthalpy recovery studies of this particular blend resulted in the thermograms shown in Figure 10, illustrating again the existence of a phase separated system. The second recovery peak manifests all the characteristics of pure nylon 12IA as can be seen in Figure 11. The T_{max} of pure nylon 12IA and the second recovery peak in the blend are virtually superimposable. The first recovery peak, representative of the nylon 3Me6T phase, has moved to a higher temperature. The slight shift of T_{ons} and T_{max} of this peak as shown in Figure 11 again signifies the existence of a nylon 3Me6T phase containing a small amount of the nylon 12IA. Exposure of this blend to a temperature greater than 190 °C had no effect on the thermograms or kinetics produced at 190 °C, signifying the formation of an equilibrium blend structure under the lower temperature conditions.

Blends Containing Nylon 12IA. It has already been shown that nylon 6IcoT and nylon 3Me6T are immiscible with nylon 12IA. The existence of two forms of nylon 6IcoTA, and their blends with nylon 12IA, did not lead to two different types of phase behavior as was noted

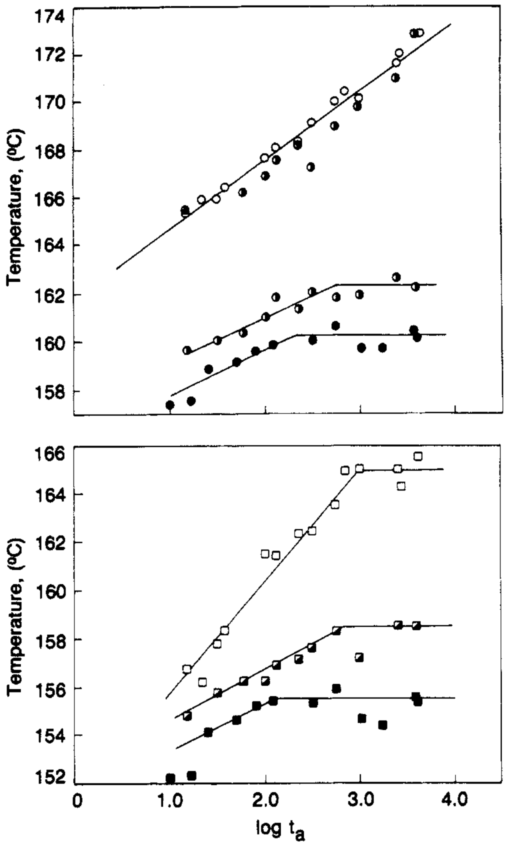


Figure 11. Aging kinetics of nylon 12IA/nylon 3Me6T blend. ○, ◐, and ●, T_{max} of nylon 12IA, blend (two recovery peaks as shown in Figure 10), and nylon 3Me6T, respectively; □, ▨, and ■, T_{ons} of nylon 12IA, blend, and nylon 3Me6T, respectively.

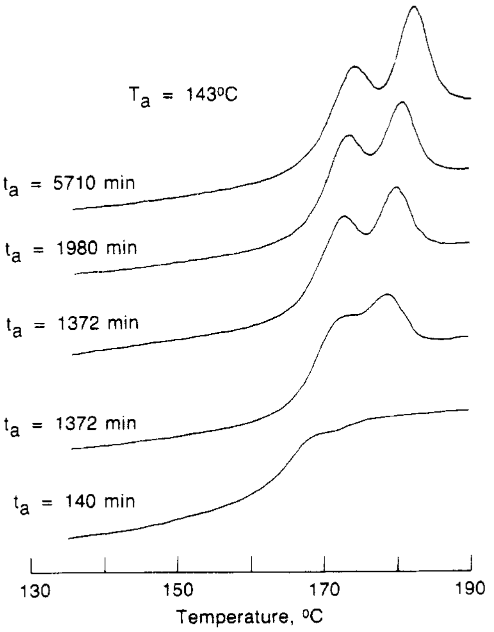


Figure 12. Representative thermograms of nylon 6IcoTA (T_g = 163.4 °C)/nylon 12IA blend.

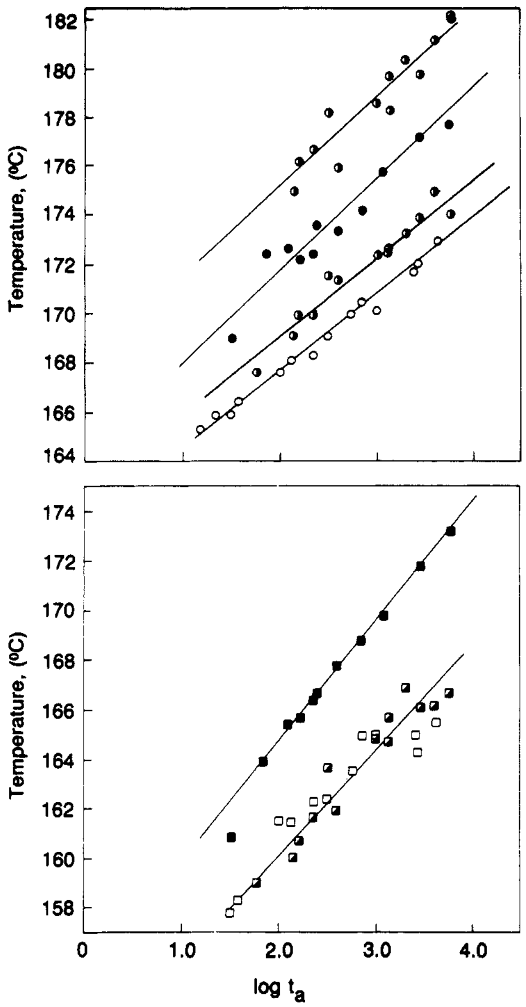


Figure 13. Aging kinetics of nylon 6IcoTA (T_g = 163.4 °C)/nylon 12IA blend: ○, ◐, and ● T_{max} of nylon 12IA, blend (two recovery peaks as shown in Figure 12), and nylon 6IcoTA, respectively; □, ▨, and □ T_{ons} of nylon 12IA, blend, and nylon 6IcoTA, respectively.

with nylon 3Me6T. Both forms of the nylon 6IcoTA were determined to be immiscible with nylon 12IA.

This may be illustrated more easily for the nylon 6IcoTA where T_g = 163.4 °C. Inspection of the thermograms shown in Figure 12 and their respective kinetics shown in Figure 13 provide vivid evidence of phase separation. There are, however, some interesting features which merit special attention. Again this blend required exposure to 230 °C in order to promote complete phase separation. Two thermograms shown in Figure 12, where t_a = 1372 min, show a distinct contrast of resolution of the recovery peaks when exposed to 190 °C/10 min and 230 °C/5 min, respectively. Perhaps the most interesting behavior noted in this blend can be seen by inspection of Figure 13. The aging kinetics, in the form of T_{max}, of the second recovery peak are shifted to a greater temperature than for the pure nylon 6IcoTA. This feature has been carefully investigated and has been determined to be a real phenomenon rather than an experimental artifact. A reason for this observation will be provided in a later section. The first recovery peak is shifted to a slightly higher temperature, symptomatic of the presence of some of the nylon 6IcoTA in the predominantly nylon 12IA phase.

A second blend of nylon 12IA, containing the nylon 6IcoTA possessing the lower T_g (T_g = 160.7 °C), presented a special problem in that not only are the respective T_g's of the two components virtually identical but also their aging kinetics were found to be very similar (see Figure 14). The recovery peak of the blend was characterized to be essentially uniform and singular irrespective of the aging time. Although not shown here, careful visual inspection of some of the recovery peaks obtained after annealing for 200–300 min identified a slight shoulder indicating heterogeneity. Exploratory studies using different values of T_a, the annealing temperature, failed to show any improvement of resolution of the antici-

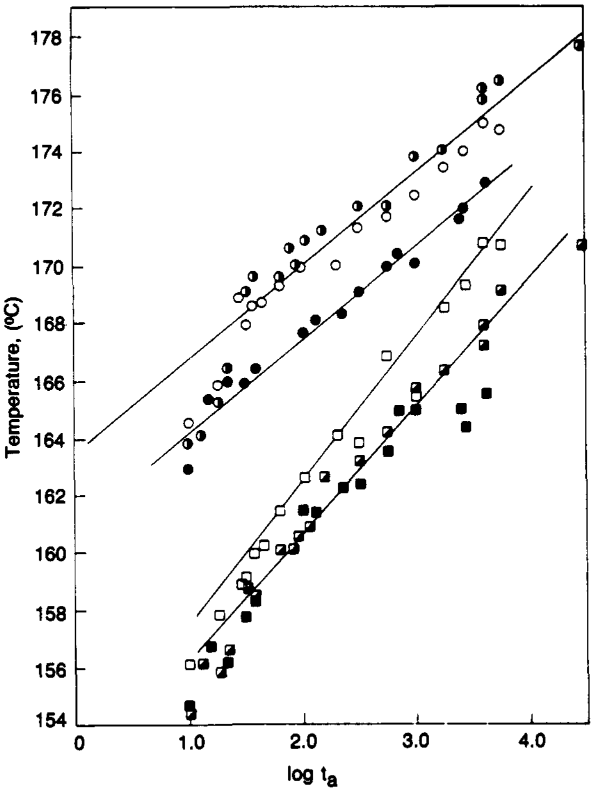


Figure 14. Aging kinetics of nylon 6IcoTA (T_g = 160.7 °C)/nylon 12IA blend: ○, ◐, and ●, T_{max} of nylon 6IcoTA, blend (one recovery peak), and nylon 12IA, respectively; □, ◪, and □, T_{ons} of nylon 6IcoTA, blend, and nylon 12IA, respectively.

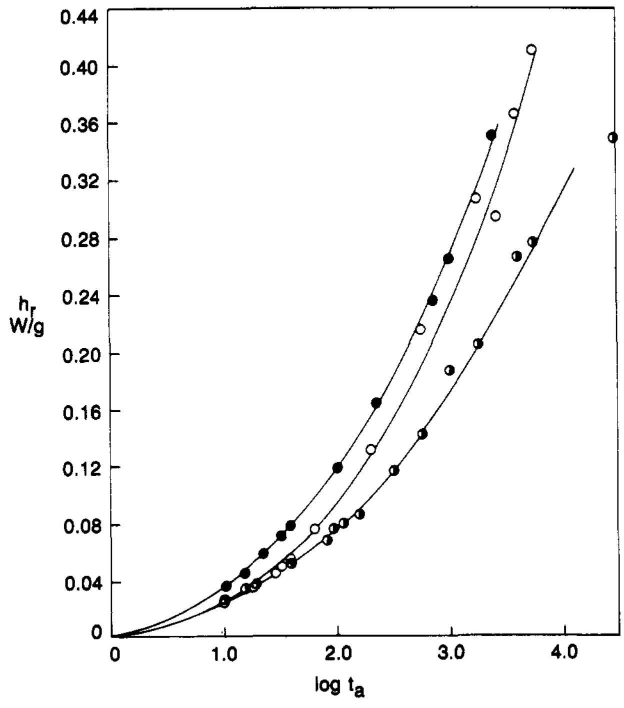


Figure 15. Recovery peak height of nylon 6IcoTA (T_g = 160.7 °C) (○), nylon 12IA (●), and their blend (50:50) (◑).

pated two recovery peaks. Careful inspection of the data shown in Figure 14, however, indicates the T_{max} to be coincident with nylon 6IcoTA but the T_{ons} to identify with the nylon 12IA. Such a situation would result if the blend thermogram was composed of two peaks of similar magnitude, superimposed one upon the other, i.e., if the blend was immiscible. Evidence to support this supposition is also provided in Figure 15 which shows the subtracted peak height h_r for the blend and the two pure polymers. The recovery peaks for the pure polymers are very similar in magnitude yet at increased values of t_a the blend recovery peak is demonstrably smaller than that of either of the two pure polymers. This situation contrasts to that shown previously for the miscible blend of nylon 3Me6T and nylon 6IcoTA (Figure 7) and could only result conceivably if the blend was imiscible. The departure from linearity of T_{max} at low values of log t_a is caused by using values obtained from thermograms subtracted from the quench-cooled thermogram.

The question of choosing the optimum temperature T_a for aging has been addressed recently.[2] In the general case, as employed here, a value of $T_a \simeq T_g - 20$ °C is most appropriate since the peak recovery height usually reaches its maximum. With respect to the position of the peak maximum, however, the situation is less clear. The relaxation time, τ, for a given polymer can be represented by eq 6.

$$\tau = A \exp\left[\frac{x\Delta h}{RT_a} + \frac{(1-x)\Delta h}{RT_f}\right] \qquad (6)$$

In this expression T_f is the fictive temperature, R is the gas constant, and x and Δh are factors that depend upon the material in question. The relaxation of enthalpy is given by an equation of the form

$$\phi(t) = \exp(-(t/\tau)^{\beta}) \qquad (7)$$

where β is again dependent upon the structure of the material. There have been attempts to correlate these various parameters with the structure of polymers.[24] However, the information gained from this analysis is still very rudimentary, and since nylon 12IA and nylon 6IcoTA are very similar in structure, it is only possible to conclude that the parameters β, x, and Δh must also be very similar. Accordingly, the magnitude of the separation of the enthalpy recovery peak for both polymers is relatively insensitive to the quantity $T_g - T_a$. This provides a sensible explanation of the lack of peak resolution for this blend irrespective of the annealing temperature. Although the peaks are not resolved, it is still possible to deduce that this blend is immiscible.

2. Correlation of Structure with Phase Behavior. The theoretical background introduced earlier provides for a quantitative evaluation of phase behavior provided that the polymers can be rationalized as $A_yB_zC_{1-y-z}$ copolymers. Although the polymers in question are composed of phenyl units of differing isomers, in terms of both quantity and category, no distinction is made within the model to account for this structural variation. The polymers also contain a great diversity of alkyl groups (see Table I); however, again no distinction will be made and all alkyl moieties (methylene, methine, methyl, and alicyclic) will be treated as equivalent to methylene units. Obviously, the contribution of the various aliphatic fragments to the volume fraction of methylene units will reflect their respective group molar volume.[25]

Using eq 5 and the segmental interaction parameters χ_{AB}, χ_{BC}, and χ_{AC} calculated for $A_yB_zC_{1-y-z}$-type copolymers[5] results in values of χ_{blend} for all the binary polymer mixtures shown in Table III. All the values calculated are positive and therefore a result clearly favoring immiscibility. This has been found to be supported in general by the experimental evidence documented previously, with two exceptions. One of these, the blend of nylon 6IcoT and nylon 6IcoTA, is in clear contradiction to the theoretical prediction. In addition to this, the blend of nylon 3Me6T and the nylon 6IcoTA has provided two different types of behavior: one miscible and the other

Table III
Summary of the Phase Behavior of Aromatic Polyamide Blends

blend	experimentally obsd phase behavior	calcd value of χ_{blend}[a]
nylon 6IcoT/nylon 3Me6T	immiscible	0.016
nylon 6IcoT/nylon 6IcoTA	miscible	0.006
nylon 6IcoT/nylon 12IA	immiscible	0.074
nylon 3Me6T/nylon 6IcoTA	immiscible/miscible	0.002
nylon 3Me6T/nylon 12IA	immiscible	0.020
nylon 6IcoTA/nylon 12IA	immiscible	0.036

[a] Using eq 5 and $\chi_{AB} = 7.982$, $\chi_{BC} = 7.46$, and $\chi_{AC} = -0.288$.

immiscible. Although no compositional variation within the nylon 6IcoTA material has been positively identified to account for these conflicting observations, it is believed that this blend resides in a borderline area. This is supported by two observations. The first one is that the immiscible nylon 3Me6T/nylon 6IcoTA blend was seen to be marginally phase separated at 190 °C. Secondly, it has been shown that the blend can be made completely miscible by only the slightest perturbation of structure such as that embodied in a small adjustment of the relative proportion of conformers making up the alicyclic component.

It is interesting to note that values of χ_{blend} for these two blends are substantially closer to zero than all the others. Consequently, the influence of the entropic contribution could be quite significant for these systems, especially in view of the current uncertainty of the scaling of the model[3-5] and the relatively low molecular weight of these polymers. Aside from this latter consideration it is believed that the principal underlying cause for miscibility in the exceptions noted is because these blends are close to an overall interactional null condition as calculated by the model, i.e., $\chi_{\text{blend}} \simeq 0$. In this special condition there are a variety of factors, outside those considered thus far, which may be responsible for miscibility in these systems. Many of these are embodied in the approximations and simplifications required to apply the model in the first place, however, their potential influence will be discussed here.

Variations of interaction resulting from structural isomerism of phenyl groups are well-known[7,26] and may be equally responsible here. This alone could account for the deviations in expected behavior. The same may also apply to the different types of alkyl fragments; however, the most noticeable feature of this simplified *mer* assignment is the treatment of an alicyclic moiety as a polymethylene sequence. This may certainly be inappropriate; however, it is believed that these potential oversimplifications are not important in polyamide blends away from the limiting condition, $\chi_{\text{blend}} \simeq 0$. There are of course more radical modifications of the basic model which can be proposed to account for the above exceptions. Presently, the model does not include any contribution from an amide-amide interaction even though such interactions probably exist. It may be argued that when the sum of the intra- and inter-molecular repulsive interactions is close to zero, then the former interactional component may exert an influence. In the general case, this contribution is insignificant and is outweighted by repulsive interactions; otherwise it could be argued that nearly all polyamide-polyamide blends should be miscible.

An alternative, and equally radical, change of direction for the model could be adopted by establishing a group contribution approach[27] based on *mer* unit surface area rather than *mer* volume, as provided by parameters calculated for UNIFAC.[28] This may be of particular value for polymers containing alicyclic moieties where the difference of mer volume between this structure and an equivalent polymethylene sequence is hardly noticeable. However, when expressed as a surface volume element then considerable differences are found. Even at this level, UNIFAC still does not provide a totally adequate evaluation of the surface area of an alicycle. Notwithstanding these important issues, the binary interaction model developed for these systems is a simple approach which still accounts for a great deal of experimental evidence. At this stage it would be undesirable to introduce a more complex foundation which may be unnecessary; particularly until more experimental data has been obtained. Aside from these more general considerations with respect to phase phenomena in this category of polyamide blends, there are two features of this study which also require additional comment. It has already been stated that an apparent geometrical isomer compositional variation of the alicyclic moiety within the nylon 6IcoTA has been identified. This may have a significant impact on the free volume or equation of state contribution to the free energy balance. Discussions concerning this contribution to the free energy of mixing are available in the literature,[29,30] and, although it is impossible to offer a precise description of how this factor is influenced by the isomer variation in the nylon 6IcoTA material, it is probable that this structural feature plays a significant role. Examples of stereoisomerism in the form of tacticity, influencing the phase behavior of blends are well documented in the literature.[31,32]

As mentioned previously, an unusual and interesting feature of the nylon 12IA/nylon 6IcoTA blend was noted as a measurable shift to higher temperature of the $T_{\max}$ of the nylon 6IcoTA phase in the blend as shown in Figure 13. It is also possible to discern a slight shift of $T_{\max}$ for the related blend, containing the lower T_g nylon 6IcoTA, as shown in Figure 14. A reasonable explanation for this unexpected phenomenon may be advanced as follows. The two materials in question must out of necessity be heterogeneous at the molecular level. The differing reactivities of the species comprising the polymerization mixture would result in a range of polymer species of different composition. This difference cannot be too great, however, or phase separation in the pure polymers would be evident.[33] It is believed that, in the blend, the nylon 12IA sequesters the molecular species that are miscible with itself leaving a nylon 6IcoTA phase of different overall composition and therefore of a slightly higher T_g. This would result in the observed shift of aging kinetics for this phase.

Conclusions

The application of a binary interaction model, established originally to describe the behavior of aliphatic/aromatic polyamide mixtures, offers a prediction of immiscibility for all the aromatic polyamide blends investigated here. This has been found to be supported by the experimental evidence in most instances and confirms the axiom that two like polymers will in general form phase separated systems. A particularly striking example illustrating this has been provided by a blend of aromatic polyamides containing alicyclic moieties, where casual inspection of their very similar chemical structures would intuitively suggest miscibility. Notable exceptions, however, have also been found suggesting that the real situation is more complex than can be currently formulated. It has been possible to offer qualitative reasoning as to why these exceptions occurred, either by examining the deficiencies of the approximations involved in applying the model or by the inclusion of additional processes such as a favorable hydrogen-bonding interaction in the special situation when the balance of intra- and intermolecular repulsive interactions is close to a null condition. Systematic investigations involving carefully designed and characterized polymers would assist in resolving some of the important but as yet unanswered questions raised here.

On a separate, but equally important note, many of the conclusions described here would not have been possible except for the emergence of a new analytical procedure. On the basis of the structural dependence of kinetics of enthalpy recovery of polymers, the technique has displayed an exceptional ability to provide detailed information on phase phenomena in the situation when the T_g's of the two components in a blend are virtually coincident. Indeed, it is probable that this procedure has been capable of determining phase behavior in the nylon 12IA/nylon 6IcoTA blend when no other technique would have been able to do so. However, a less positive identification would only have been permissible had this particular blend been miscible. It is also believed that there are general applications of this technique in the study of partial miscibility and interfacial phenomena. As in previous work much of the information has been obtained from characterizing the position of the enthalpy recovery peak, however, it has also been shown for the first time that the height of the peak contains important information which can be used to delineate phase behavior.

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Registry No. Trogamid T, 9071-17-4; Zytel 330 (copolymer), 25750-23-6; Zytel 330 (SRU), 58814-83-8; Bexloy APC-803, 26742-97-2; Grilamid TR55, 79331-75-2