The effect of physical interactions on melt-phase homogenization of mixtures of poly(*m*-xylene adipamide) with aliphatic polyamides induced by interchange reactions

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Poly(*m*-xylene adipamide) (MXD6) was melt mixed at 290°C in a Brabender with the aliphatic polyamides: nylon-6,6, nylon-6,9, nylon-6,10, nylon-6,12 and nylon-12,12. MXD6 was found to be physically immiscible with each nylon-*x*,*y*; however, owing to interchange reactions during melt mixing, the mixtures eventually became one-phase. The time required for this reaction-induced phase homogenization was followed visually and by differential scanning calorimetry (loss of ability to crystallize and change in glass transition behaviour) and was found to increase significantly as the ratio of methylene to amide units, CH_2/NHCO ratio, in the aliphatic polyamide increased. The extent of reaction at the point of phase homogenization was determined by ^1H nuclear magnetic resonance, and this, too, increased with the CH_2/NHCO ratio but not as much as the melt mixing time required for phase homogenization. These effects are attributed to the more unfavourable polymer–polymer interaction energy between MXD6 and nylon-*x*,*y* as the CH_2/NHCO ratio increases. This physical parameter is believed to influence the initial interfacial area (through the interfacial tension), the initial interfacial thickness and the length of the critical copolymer segment length for conversion of a microphase-separated block copolymer to a single-phase melt. All these factors influence the melt mixing time required for phase homogenization.

(Keywords: blends; polyamides; interchange reactions; phase homogeneity; copolymers)

INTRODUCTION

There is a growing body of literature on binary mixtures of different polyamides[1–14]. An important issue is the phase homogeneity of these materials, which may stem from physical miscibility or from interchange reactions leading to copolymer formation. In a recent paper[1] we described the phase homogenization of physically immiscible mixtures of poly(*m*-xylene adipamide) (MXD6) and nylon-6 via interchange reactions during melt mixing[15–17]. This paper explores this process in mixtures of MXD6 with a series of aliphatic polyamides of the type nylon-*x*,*y*. The purpose is to demonstrate that the magnitude of the physical polymer–polymer interaction energy density B, or the related Flory–Huggins interaction parameter χ ($\chi = BV_r/RT$, where V_r is an arbitrary reference volume), influences the extent of reaction and the time to achieve a single-phase melt, i.e. phase homogenization. As the interaction energy becomes larger (more unfavourable for miscibility), we expect both the reaction time and the extent of reaction needed for phase homogenization to increase for the reasons outlined below.

BACKGROUND

If two condensation polymers are physically immiscible, then any interchange reactions between them during melt mixing are initially limited to the interfacial zone where the two types of segments can mix. Thus, the progress of the reaction depends on the interfacial area and the thickness of the interface, both of which can be related to the physical polymer–polymer interaction energy, as shown next.

If we assume for simplicity that one of the polymers forms a dispersed phase of spherical particles (radius R), then the interfacial area per unit volume, S, is related to this measure of size by:

$$S \sim 1/R \qquad (1)$$

Based on principles of fluid drop break-up in flow fields dating back to the initial theory by Taylor[18], correlations for particle size during mixing of polymers with the following form have been developed[19–23]:

$$\eta_m RG/\gamma = F(\eta_d/\eta_m) \qquad (2)$$

where γ is the interfacial tension, G the shear rate, η_m the viscosity of the matrix phase and η_d the viscosity of the dispersed phase. Thus, when all other factors are the same, particle size is directly proportional to interfacial

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tension:

$$R \sim \gamma \tag{3}$$

Recently, mean-field theories of the polymer–polymer interface have been developed in terms of the Flory–Huggins interaction parameter χ. These theories[24–29] and available experimental evidence[30,31] indicate that the polymer–polymer interface is diffuse and can be characterized by a thickness λ where the segments of the two polymer types are mixed. The theory of Helfand and coworkers[24–26] gives:

$$\gamma = (kT/a)(m\chi)^{1/2} \tag{4}$$

$$\lambda = 2(m\chi)^{-1/2} \tag{5}$$

where a and m are physical parameters. A similar theory by Roe[28] leads to different powers of χ, i.e.

$$\gamma \sim \chi^{3/4} \tag{6}$$

$$\lambda \sim \chi^{-1/4} \tag{7}$$

As the polymer–polymer interaction is more unfavourable, the interfacial contact will be less and the interfacial compositional gradient will be sharper, i.e. less mixing per unit area of contact.

As a first approximation, the fraction of the mixture volume that the interfacial zone of mixed segments initially occupies is proportional to the product of S and λ. Using equation (2) leads to:

$$S\lambda \sim \lambda/R \sim \lambda/\gamma \tag{8}$$

Thus, regardless of whether the Helfand or Roe versions of the theory for the interface are used, we have:

$$S\lambda \sim 1/\chi \sim 1/B \tag{9}$$

As the interaction energy becomes more positive or unfavourable for mixing, the volume fraction of the zone where interchange reaction can occur decreases. These comments apply to the situation in the initial stages of reaction before the interface is perturbed by formation of copolymer. The reaction will broaden the interface and increase the opportunity for further reaction.

The interaction energy influences the process of phase homogenization in yet another way, viz. the extent of reaction needed to produce a single-phase melt. The Flory–Huggins theory[32] predicts that a blend of two polymers A and B (each of molecular weight M and density ρ) having a positive interaction energy density B will form a single-phase mixture at temperatures above an upper critical solution temperature given by:

$$T_c = \frac{BM}{2\rho R} \tag{10}$$

If a single interchange reaction occurs mid-chain, thus transforming each molecule into a diblock copolymer, then according to the theory of Leibler[33] the critical temperature to achieve a single phase is reduced by a factor of 5.25, i.e.

$$T_c = \frac{BM}{10.5\rho R} \tag{11}$$

While a complete theory is not yet available, it is clear that multiple interchange reactions per molecule will lower the temperature for phase hydrogenization even further. Thus, the larger the positive value of B, then the more interchange reactions (or the shorter the block segment length) needed to cause phase homogenization at a fixed temperature. Ultimately, interchange reactions will lead to a completely random copolymer. Prior to this, the mixture will lose all ability to crystallize as the segments become shorter and shorter. A homogeneous melt or a single T_g may be achieved before the ability to crystallize is lost[1,34] depending on the interaction between the two types of segments.

It is intuitively expected that the physical interaction between MXD6 and nylon-*x,y* will become more unfavourable as the aliphatic hydrocarbon content of the latter, or the $CH_2/NHCO$ ratio, increases. However, this point can be placed on a more quantitative basis using the recent work of Ellis[2–8]. He has examined the miscibility using solution precipitation procedures, i.e. in the absence of interchange reactions, of various aliphatic polyamides of the type employed here with the partially aromatic polyamide:

$$-\!\!\{CO\text{-}C_6H_4\text{-}CONH(CH_2)_6NH\}\!\!- \tag{12}$$

He has used a binary interaction model[35–37] to describe how the Flory–Huggins interaction parameter depends on the $CH_2/NHCO$ ratio, and obtained the result[7] reproduced here as the lower curve in *Figure 1*. Because of the potential differences in physical interaction caused by isolating the amide linkages and the phenylene rings by CH_2 units, it would not be surprising that there are some differences in the net interaction of aliphatic polyamides with MXD6 compared to poly(hexamethylene phthalamide) even though both are partially aromatic polyamides having the same number of methylene, phenylene and amide groups in their repeat units[2,6]. One manifestation of this is that MXD6, unlike poly(hexamethylene phthalamide), is not miscible with nylon-6 or nylon-6,6. Consequently, the interaction parameter for MXD6 mixtures with aliphatic polyamides is not negative at $CH_2/NHCO = 5$. By adjustments of

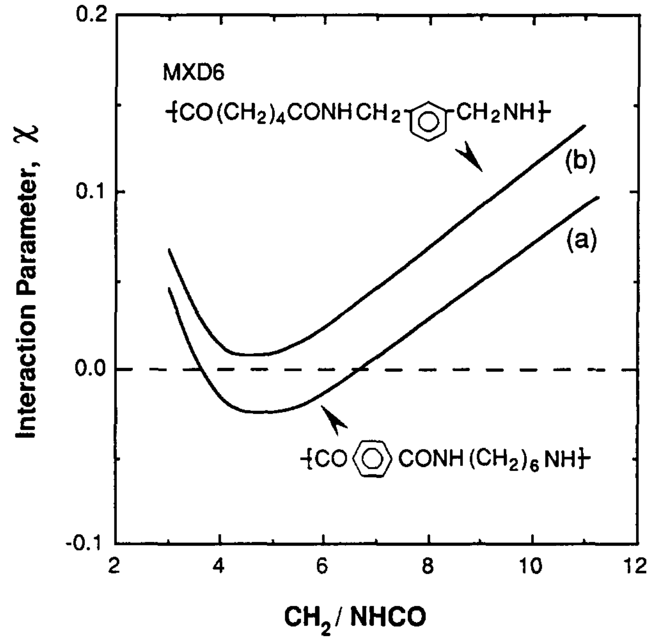

Figure 1 Interaction parameters for partially aromatic polyamide/aliphatic polyamide mixtures as a function of the $CH_2/NHCO$ ratio in the aliphatic polyamide: (a) results reported by Ellis[7] for poly(hexamethylene phthalamide) mixtures and (b) an estimate for MXD6 mixtures using an arbitrarily adjusted value of the methylene–phenylene interaction parameter (see text for explanation)

the interaction parameters in the model used by Ellis[7] (e.g. changing the χ_{ij} for the methylene–phenylene interaction from -0.288 to 0.1), the net interaction curve will shift to slightly positive values at CH_2/NHCO = 5 without any major change in overall shape. The upper curve in *Figure 1* is such an adjusted calculation, and we suggest that qualitatively a similar curve ought to describe the interaction of MXD6 with aliphatic polyamides. The main point is that the polymer–polymer interaction energy (B or χ) becomes more positive as the CH_2/NHCO ratio increases from that of nylon-6,6.

EXPERIMENTAL

The various polyamides used here were obtained from commercial sources (see *Table 1*). Each aliphatic polyamide was melt mixed with MXD6 in a Brabender Plasti-Corder for varying periods of time at 290°C using a rotor speed of 60 rpm. The MXD6/aliphatic polyamide ratio was fixed at 50/50 by weight throughout this work. All samples were dried in a vacuum oven at 80°C for more than 12 h before each melt mixing procedure. Solution-precipitated mixtures of MXD6 and nylon-6,6 were also prepared by dissolving in trifluoroethanol and precipitation by pouring into diethyl ether.

Thermal analyses were conducted in a N_2 atmosphere using a Perkin–Elmer differential scanning calorimeter, DSC-7, with heating and cooling at 20°C min^{-1} between 0 and 290°C. The thermal properties were recorded during a second scan. The glass transition temperature T_g values were computed by the midpoint method. The breadth of the glass transition region, ΔT_g, was used to determine the phase homogenization time as described previously[1]. The ΔT_g is defined as the span from the initial onset of the glass transition region to its completion whether there is one or two transitions. The melting point was taken as the maximum of the d.s.c. endothermic peak. The combined heat of fusion ΔH was obtained by integration from 100 to 270°C, which includes the melting of both species. In some cases, crystallization was observed on heating in second scans, and the area of this exotherm was subtracted from the melting endotherms to give the initial ΔH.

Proton nuclear magnetic resonance (General Electric NT-360) was used to investigate the extent of interchange reactions in the MXD6/aliphatic polyamide mixtures. Samples for n.m.r. analysis were dissolved in deuterated trifluoroacetic acid (TFA-d) to 0.14% (w/v). Chemical shifts were referenced to tetramethylsilane (TMS) in dimethylsulphoxide (DMSO) solution.

THERMAL ANALYSIS FOR PHASE HOMOGENIZATION

All of the MXD6/aliphatic polyamide mixtures examined here were opaque or immiscible in the initial stages of melt mixing; however, these mixtures become transparent after further mixing. The time to become transparent was observed to increase as the CH_2/NHCO ratio in the aliphatic polyamide increased, as anticipated above.

This visual change of the melt in the Brabender was further examined by thermal analysis. *Figure 2* shows how d.s.c. thermograms for 50/50 MXD6/aliphatic polyamide mixtures change with melt mixing time. For each system, both melting points and the heat of fusion decrease with mixing time in the Brabender. *Figure 3* shows the glass transition temperature regions expanded from *Figure 2*. Initially, the thermograms show two T_g values, which come closer with increased mixing time, and finally there is one T_g at about the time when transparency was observed in the Brabender. *Figures 4* to *6* summarize the results of these thermal analyses. *Figure 4a* shows that the melting point of the MXD6 component systematically decreases with mixing time in the Brabender. The rate of decrease is greatest for nylon-6,6 and becomes slower as the CH_2/NHCO ratio of the aliphatic polyamide component increases. The melting-point depression of the aliphatic polyamides follows a similar trend as shown in *Figure 4b*. The melting points of the pure aliphatic polyamides vary according to their molecular structures[38,39] *Figure 5* shows the change in the combined heats of fusion for these polyamide mixtures with mixing time. The rate at which ΔH decreases becomes slower as the CH_2/NHCO ratio in the aliphatic polyamide increases. These thermal analyses reflect the state of the polyamide crystals, which involves a number of complex issues, e.g. the actual *versus* the equilibrium melting points of polymer crystals[40,41] plus the melting-point depression of blends[42–46] and of copolymers[47–49].

Figure 6 shows the glass transition temperatures of mixtures of 50% MXD6 with the various aliphatic polyamides taken from *Figure 3*. The two T_g values observed in the initial stage of melt mixing merge into one after sufficient mixing in the Brabender. The time to

Table 1 Polyamides used in this study

Polyamide	CH_2/NHCO ratio	Molecular weight, $\bar{M}_n$	Relative melt viscosity[a]	T_g[b] (°C)	T_m[b] (°C)	Source
Poly(*m*-xylene adipamide) (MXD6)	–	25 300[c]	1.0	90	235	Mitsubishi Gas Chemical Co.
Nylon-6,6	5	n.a.[d]	1.3	57	261	E. I. du Pont Co.
Nylon-6,9	6.5	n.a.	1.4	37	210	Aldrich Chemical Co.
Nylon-6,10	7	n.a.	1.3	38	219	Aldrich Chemical Co.
Nylon-6,12	8	n.a.	1.4	38	216	E. I. du Pont Co.
Nylon-12,12	11	n.a.	1.7	33	181	E. I. du Pont Co.

[a] Brabender torque at 290°C and 60 rpm after 10 min divided by that of MXD6

[b] From second d.s.c. scan with heating and cooling at 20°C min^{-1} (T_g = midpoint, T_m = peak maximum)

[c] End-group concentrations are NH_2 = 12 and COOH = 67 μeq/g

[d] Not available

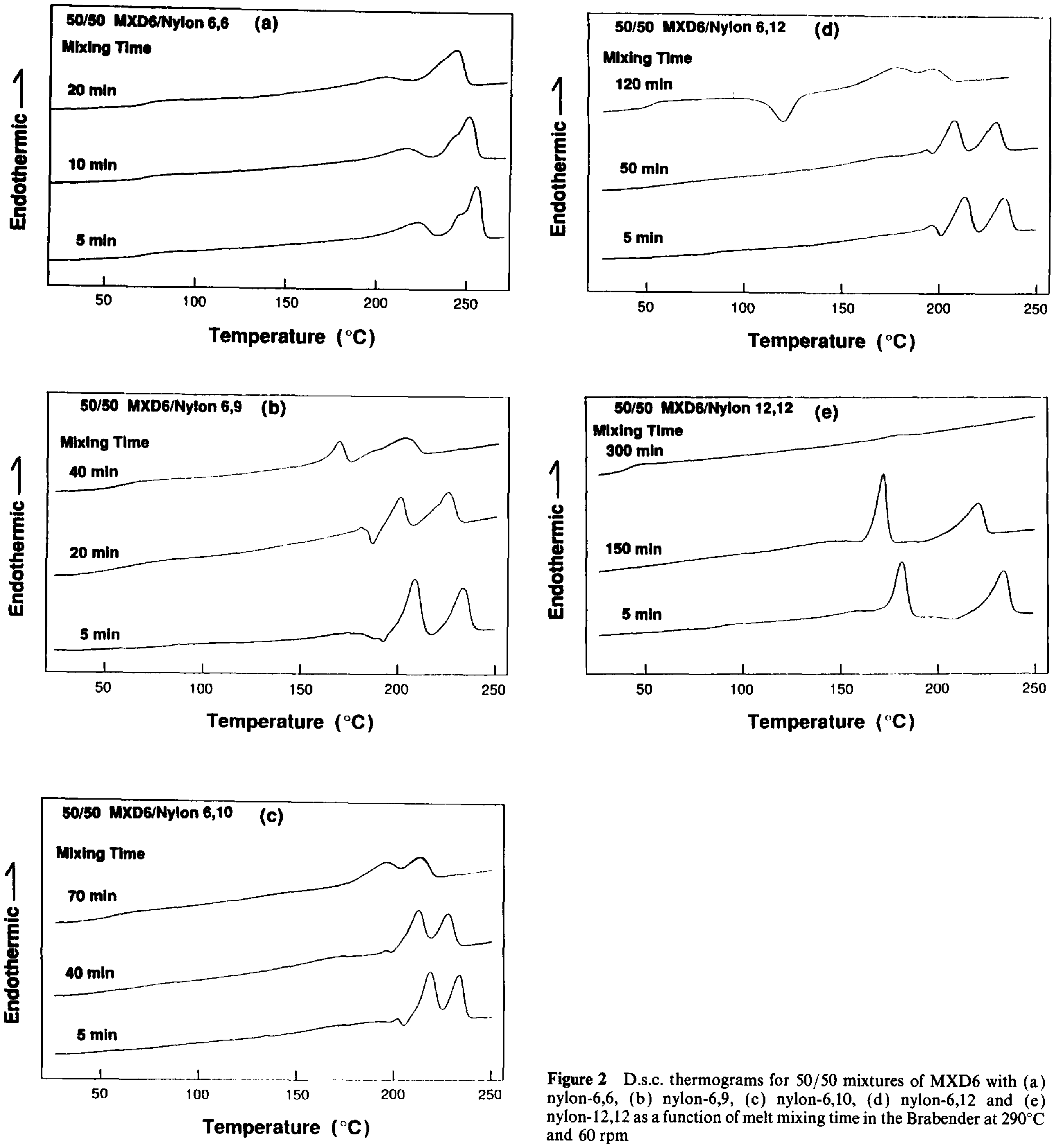

Figure 2 D.s.c. thermograms for 50/50 mixtures of MXD6 with (a) nylon-6,6, (b) nylon-6,9, (c) nylon-6,10, (d) nylon-6,12 and (e) nylon-12,12 as a function of melt mixing time in the Brabender at 290°C and 60 rpm

reach this point differs from the time where ΔH goes to zero, but it too increases with the $CH_2/NHCO$ ratio of the aliphatic polyamide. MXD6 is obviously immiscible with aliphatic polyamides having $CH_2/NHCO > 6.5$ in the initial stages of melt mixing at 290°C. However, there is some question about the miscibility of MXD6 with nylon-6,6, since this mixture shows one T_g after the shortest melt mixing time, about 5 min. *Figure 7* shows d.s.c. thermograms for a solution-prepared 50/50 MXD6/nylon-6,6 mixture (lower curve) and for a control sample that had been melt mixed, dissolved and then precipitated using the same procedure (upper curve). The latter shows a single T_g while the former, which has had no thermal opportunity for interchange reaction, shows two broadened T_g values. These results suggest that MXD6/nylon-6,6 mixtures are close to being miscible as reported[1] for MXD6/nylon-6 but are not completely so. The middle curve in *Figure 8* shows the glass transition temperature of 50/50 MXD6/aliphatic polyamide mixtures after phase homogenization. The upper and lower curves are the glass transition temperatures of the pure polyamides after mixing in the Brabender for the same length of time required to achieve phase homogenization of their mixtures. The T_g of MXD6 tends to decrease slightly with mixing time at 290°C, which reflects some thermal degradation. Interestingly, the T_g of the mixture after phase homogenization tends to deviate significantly from linear additivity, and the

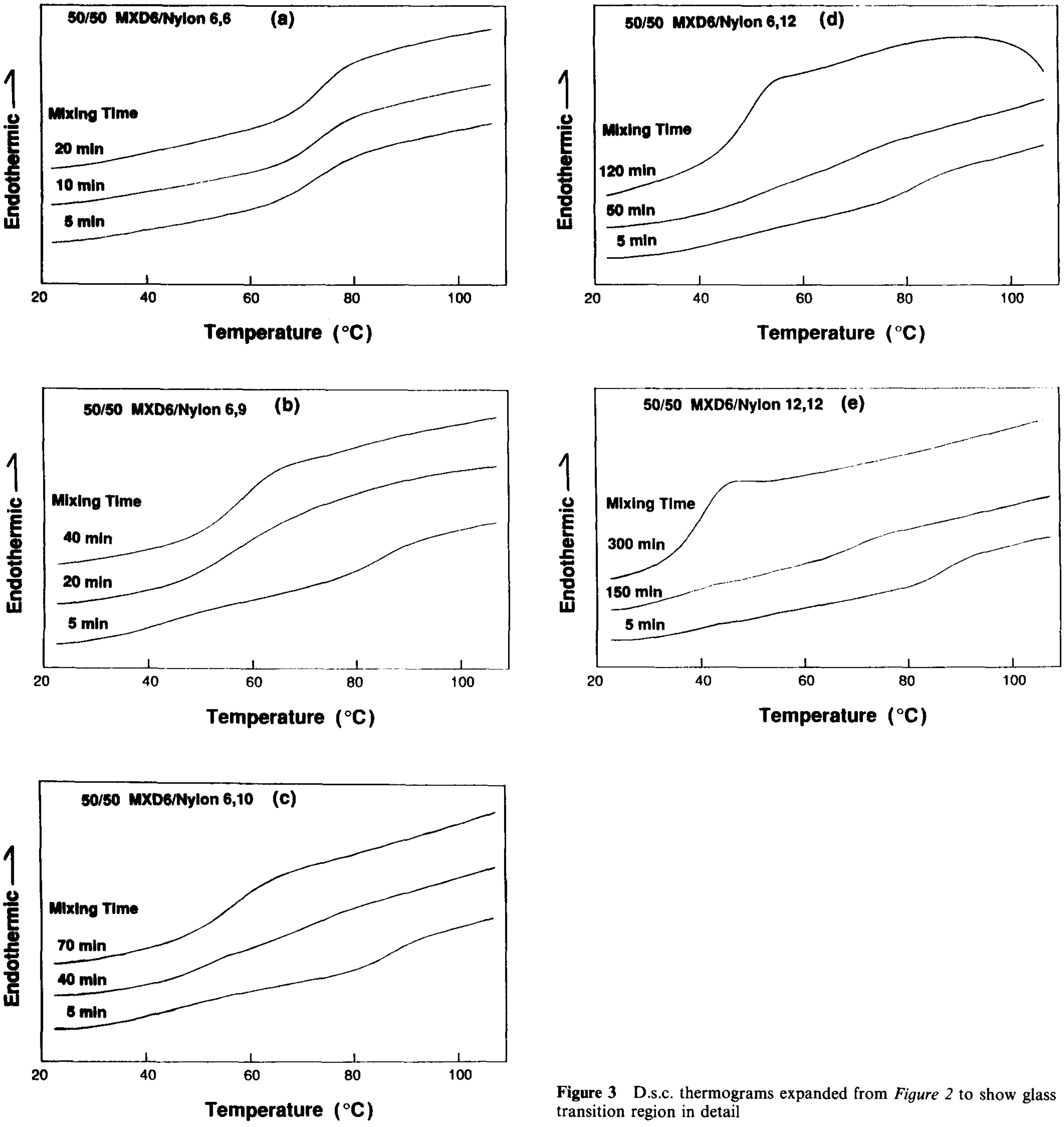

Figure 3 D.s.c. thermograms expanded from *Figure 2* to show glass transition region in detail

deviation increases with the CH_2/NHCO ratio in the aliphatic polyamide. Similar deviation of T_g has also been reported for physically miscible polyamide/polyamide mixtures[9]. Several factors may contribute to the current observation, including disruption of short-range order that could affect hydrogen bonding, block segment length shortened by interchange reactions, and thermal degradation.

Figure 9 shows how the breadth of the glass transition temperature region, ΔT_g, obtained from the d.s.c. thermograms, decreases with mixing time. The time for phase homogenization, defined as the point when ΔT_g approaches its final constant value[1], dramatically increases as the CH_2/NHCO ratio of the aliphatic polyamide becomes larger, as shown in *Figure 10*.

NUCLEAR MAGNETIC RESONANCE ANALYSIS FOR INTERCHANGE REACTIONS

The extent of interchange reaction required to achieve phase homogenization was investigated using n.m.r. *Figure 11* shows the n.m.r. spectra for each mixture at a point just after phase homogenization has occurred. A new peak appears in the vicinity of the peak at 4.68 ppm attributed to the methylene group between the phenylene ring and the amide group in MXD6[1]. Interestingly, the new peak for these mixtures is observed downfield of the 4.68 ppm peak, whereas it was observed upfield of this for MXD6/nylon-6 mixtures[1]. This difference in position of the new peak may be due to a solvent effect. Nylon-6 is not completely soluble in TFA-d, which leads to some

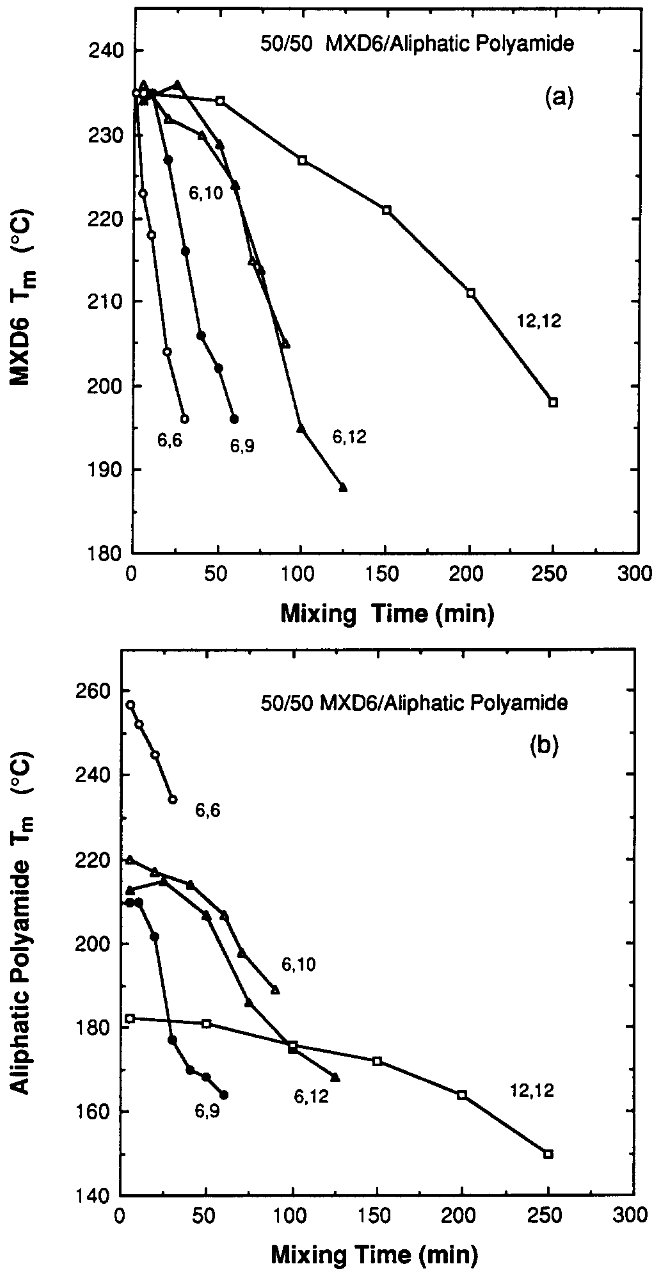

Figure 4 Melting points from d.s.c. for (a) MXD6 and (b) aliphatic polyamide in 50/50 MXD6/aliphatic polyamide mixtures as a function of melt mixing time in the Brabender at 290°C and 60 rpm

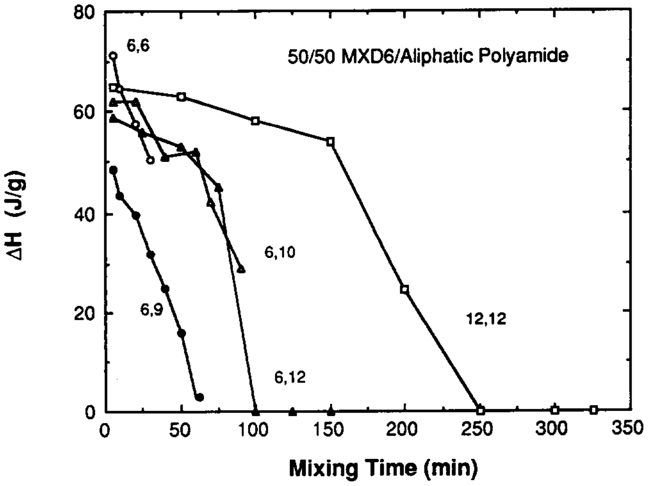

Figure 5 Combined heats of fusion for 50/50 mixtures of MXD6 with aliphatic polyamides as a function of melt mixing time in the Brabender at 290°C and 60 rpm

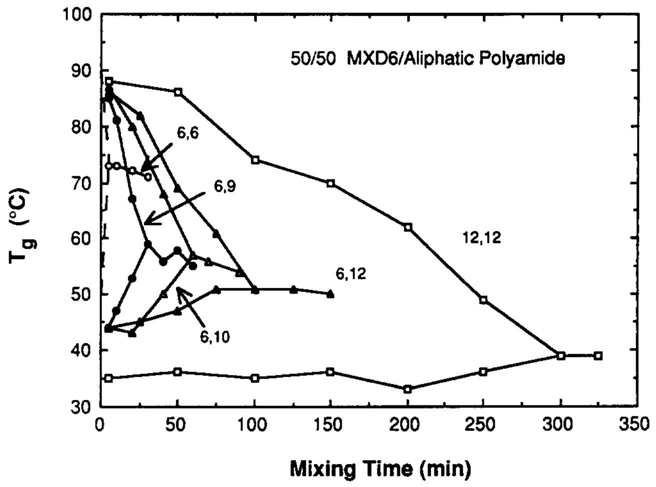

Figure 6 Glass transition temperatures for 50/50 mixtures of MXD6 with aliphatic polyamides as a function of melt mixing time in the Brabender at 290°C and 60 rpm

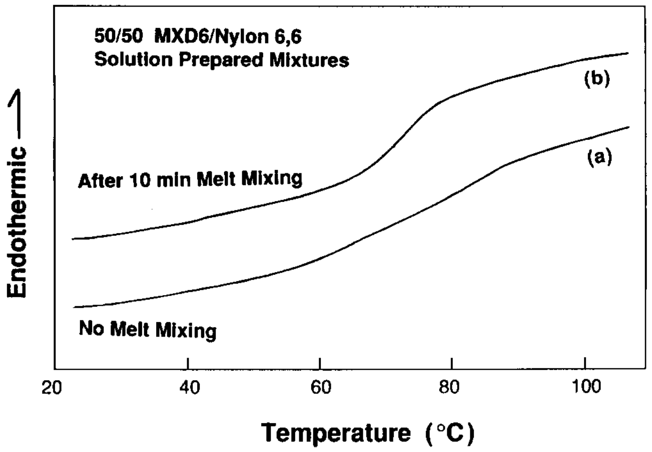

Figure 7 D.s.c. thermograms of solution-prepared 50/50 MXD6/nylon-6,6 mixtures: (a) without any melt mixing; and (b) after 10 min melt mixing in the Brabender at 290°C and 60 rpm

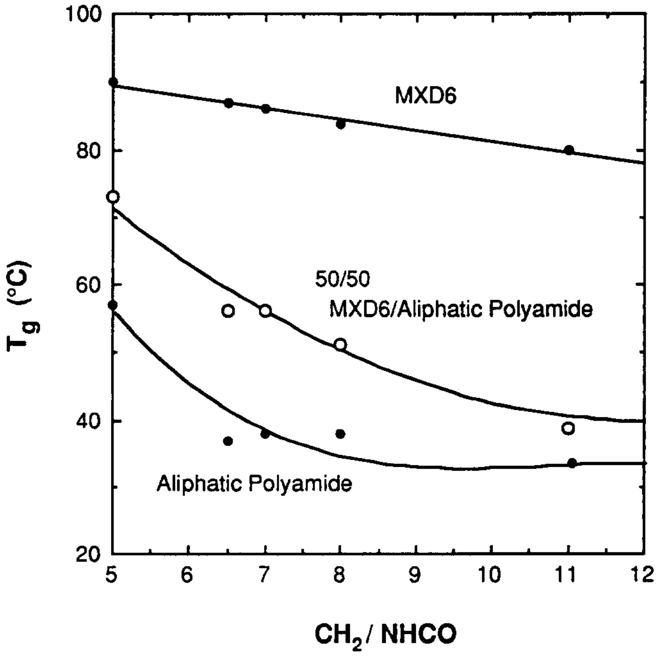

Figure 8 Glass transition temperatures of phase-homogenized 50/50 mixtures of MXD6 with aliphatic polyamides as a function of the $CH_2/NHCO$ ratio

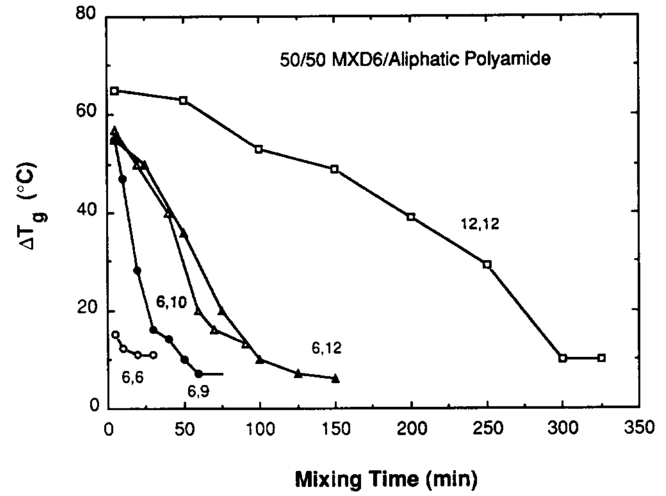

Figure 9 Breadth of the glass transition temperature region for 50/50 MXD6/aliphatic polyamide mixtures as a function of melt mixing time in the Brabender at 290°C and 60 rpm

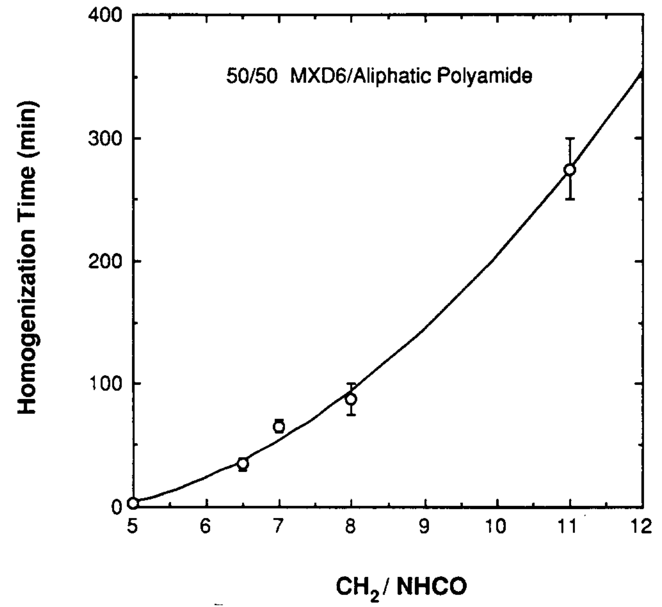

Figure 10 Phase homogenization time as a function of the CH_2/NHCO ratio for mixtures of aliphatic polyamides with MXD6

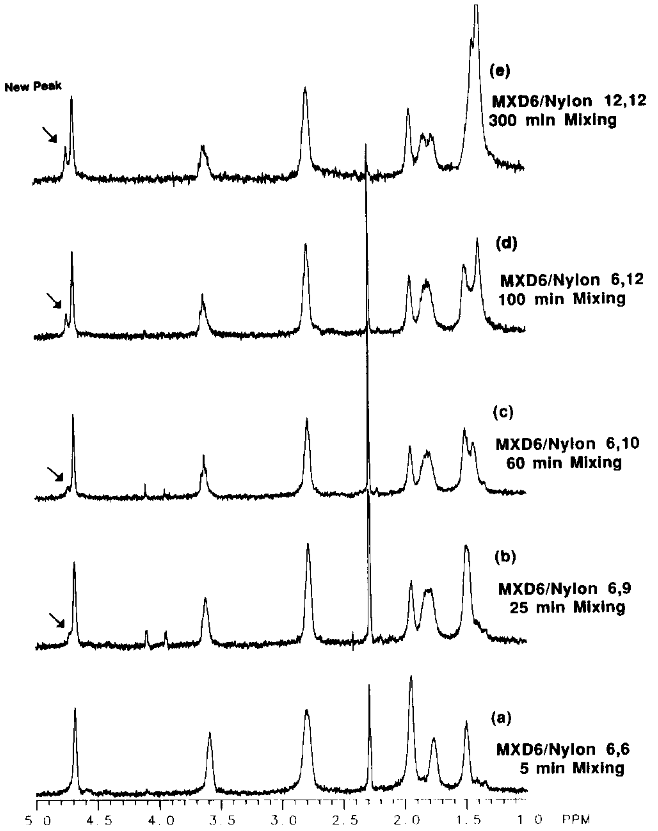

Figure 11 ^1H n.m.r. spectra in TFA-d for 50/50 mixtures of MXD6 with (a) nylon-6,6, (b) nylon-6,9, (c) nylon-6,10, (d) nylon-6,12 and (e) nylon-12,12 just after phase homogenization has occurred

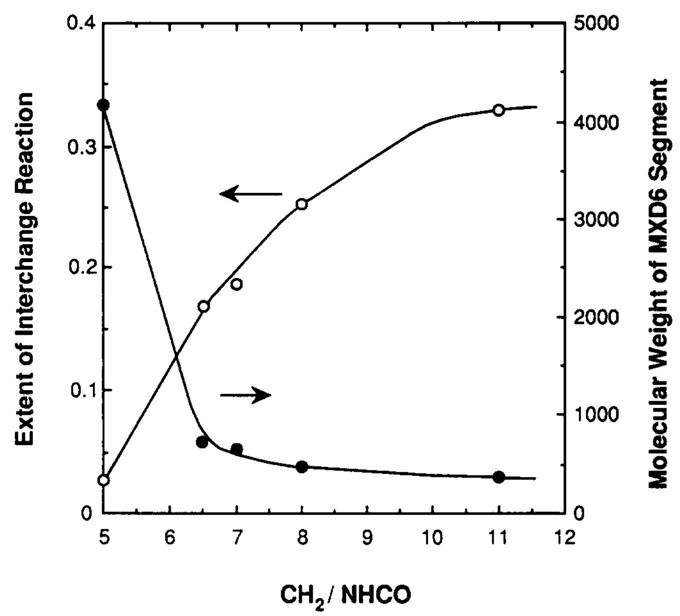

Figure 12 Extent of interchange reaction and molecular weight of MXD6 segments as a function of the CH_2/NHCO ratio at the point of phase homogenization

peak broadening[1], whereas the current polyamides are fully soluble, as may be seen by very sharp n.m.r. peaks in *Figure 11*. In any case, we believe this new peak is a consequence of the interchange reactions between MXD6 and the aliphatic polyamides, since it is not observed in pure MXD6 after 100 min of mixing in the Brabender. Unfortunately, the new peak could not be observed in MXD6/nylon-6,6 mixtures even after 30 min of mixing. The new peak tends to shift to lower magnetic field as the CH_2/NHCO ratio increases in the aliphatic polyamide (see *Figure 11*), so it is masked in MXD6/nylon-6,6 mixtures by the same adipic acid units that occur in MXD6 molecules. *Figure 12* shows the extent of interchange reaction, calculated from the hydrogen integral of the n.m.r. spectra in *Figure 11* using the method outlined in a previous paper[1], as a function of CH_2/NHCO for the aliphatic polyamide. This quantity approximates the fraction of the MXD6 amide linkages that have undergone interchange reaction. The value shown at a ratio $CH_2/NHCO = 5$ is that for a MXD6/nylon-6 mixture since MXD6/nylon-6,6 mixtures could not be so analysed, as mentioned before. *Figure 12* also shows the molecular weight of MXD6 segments of the copolymer at the point where phase homogenization occurs. The latter quantity was calculated from the extent of interchange reaction and the initial molecular weight of MXD6 (i.e. $\bar{M}_n = 25\,300$ or 200 amide linkages per molecule). It is clear from the n.m.r. results in *Figure 12* that a greater extent of interchange reaction is needed to yield a copolymer of MXD6 and nylon-*x*,*y* with one amorphous phase the larger the CH_2/NHCO ratio for the aliphatic polyamide. This is the result of the phenomenon mentioned in connection with the discussion of equations (10) and (11) and the effect of CH_2/NHCO ratio on the polymer–polymer interaction energy B (or χ).

It is interesting to compare the shapes of the melt mixing time (*Figure 10*) and the interchange reaction ratio (*Figure 12*) required for phase homogenization as a function of the CH_2/NHCO ratio. As the aliphatic polyamide component contains more CH_2 groups in its repeat unit, even more time is required to achieve a single-phase copolymer than would be expected from the increase in reaction extent needed. This is a consequence of the phenomenon mentioned in connection with the discussion of equations (1) to (9). The more unfavourable the polymer–polymer interaction energy becomes, the less opportunity there is for interchange reaction because of the more limited mixing of the two types of segments.

Finally, we should mention that the mixing intensity also affects the progress of the reaction because of the rate of surface area generation and renewal. For example, when MXD6 and nylon-6,12 are mixed in the Brabender, it takes 90 min to achieve phase homogenization. However, without any mechanical mixing, the same pair takes 1200 min to become homogeneous at 290°C. The latter experiment was done in the d.s.c. similar to the ones reported for MXD6/nylon-6 mixtures in the previous paper[1].

CONCLUSIONS

The partially aromatic polyamide MXD6 is physically immiscible with all of the nylon-*x*,*y* materials listed in *Table 1*. However, by melt mixing at 290°C these mixtures undergo interchange reactions to produce copolymers, and eventually form a homogeneous, single-phase melt that has a single glass transition when cooled. This occurs well before the point at which completely random copolymers are formed. In fact, in some cases, this condition can be reached before the segments of the two polyamide types become too short to crystallize[1,34].

The ^1H n.m.r. results show that the extent of interchange reaction required for melt-phase homogenization increases as the CH_2/NHCO ratio of the aliphatic polyamide becomes larger. However, the melt mixing time required to achieve this state (as determined by T_g behaviour) increases even more rapidly with CH_2/NHCO ratio than the critical extent of interchange reaction would suggest. All of these facts can be simply rationalized by the plausible assumption (supported by extensive results reported by Ellis[7]) that the physical segmental interaction energy, B or χ, between MXD6 and nylon-*x*,*y* increases as the CH_2/NHCO ratio for the aliphatic polyamide increases. This causes the initial interfacial tension to become higher and the interfacial thickness to become smaller, both of which reduce the volume available where the two types of segments are mixed and interchange reactions can occur. In addition, as the interaction energy becomes more unfavourable for mixing, the length of the two types of segments in the block copolymers formed must become shorter (i.e. more reaction) in order for a homogeneous melt to form. These three factors combined impose a strong physical effect on whether phase homogenization of two potentially reactive condensation copolymers will occur in a given situation or not, in addition to any effects of intrinsic chemical reactivity.

For future work, it would be interesting to explore the chemical effects caused by polyamide end-group content and to observe experimentally the spatial changes in homogeneity using an appropriate scattering technique.

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