Phase homogenization of mixtures of poly(*m*-xylene adipamide) and nylon 6 by interchange reactions

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Melt blends of poly(*m*-xylene adipamide) and nylon 6 prepared by extrusion at 260°C have two glass transitions and are opaque, whereas similar preparation at 290°C yields transparent melts and materials with a single glass transition. This phase homogenization has been shown by thermal, dynamic mechanical, and nuclear magnetic resonance analyses to be the result of interchange reactions. A single phase develops after as few as five interchange reactions per molecule. This segmented block structure explains the high level of crystallinity that is retained after phase homogenization. Such behaviour is possible when the unreacted components have an unfavourable but small interaction energy density, i.e. near miscibility, as argued using thermodynamic theories. Retention of crystallinity is useful for certain property considerations.

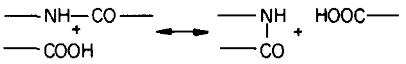
(Keywords: blends; polyamides; interchange reactions; phase homogeneity; copolymers)

INTRODUCTION

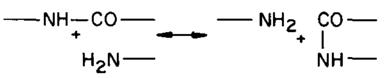
Recent literature contains numerous reports on miscibility[1–6], chemical reactions[7–13] and rubber toughening[14–18] of blends containing polyamides. In this and a subsequent paper[19], all three topics are considered. Here, we describe the phase behaviour of binary blends of nylon 6 and a partially aromatic polyamide, poly(*m*-xylene adipamide) (MXD6), as a function of thermal history that may permit interchange reactions. Our subsequent paper[19] examines the mechanical behaviour of nylon 6/MXD6 blends toughened by addition of a maleated elastomer phase.

Several reports have described miscible blends where at least one component is a polyamide[1–6]. Of particular relevance here are the examples involving mixtures of aromatic nylons with various aliphatic nylons[1–3]. These findings have been rationalized using a mean field binary interaction model[1] while others discuss the possibilities for cross-hydrogen bonding[2]. It is also now well-known that interchange reactions in blends of condensation polymers, e.g. polyester/polyester[20–24] and polyester/polyamide[25,26] systems, may play an important role in their observed phase homogeneity in addition to thermodynamic interactions. Very little information is available in the literature about interchange reactions in polyamide/polyamide blends[7]; although, clearly the following possibilities exist:

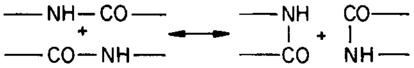
acidolysis



aminolysis



amidolysis



Such reactions are shown here to be the cause for homogeneous, single glass transition temperature (T_g) blends of nylon 6/MXD6 prepared under certain melt processing conditions.

Quite often phase homogenization caused by interchange reactions results in a significant decrease in crystallizability because the material approaches a random copolymer. However, for unreacted polymer pairs that have only a slightly unfavourable interaction energy, relatively few reactions per chain to form a segmented block copolymer may be enough to give a single phase melt that can still crystallize because of the long uninterrupted blocks of each type. Evidently this is the case for nylon 6/MXD6 blends as shown here using various techniques. Such crystallizable mixtures form a unique base polyamide for rubber toughening as described in our subsequent paper[19].

EXPERIMENTAL

The nylon 6 was obtained from Allied Signal (Capron 8207F, $M_n = 25\,000$) while the MXD6 nylon was from Mitsubishi Gas Chemical (MXD6 6007, $M_n = 25\,300$).

Blends were prepared by melt mixing and by solution methods. Melt blends were prepared in a single screw extruder (Killon, 2.54 cm diameter) at either 260 or 290°C. Solution blends were made by dissolving both polymers in the common solvent trifluoroethanol (TFE) followed by coprecipitation of the components into diethyl ether. In some cases, samples that had been melt blended first were then solution blended. Every sample was dried in a vacuum oven at 80°C for 12 h or more before each blending procedure.

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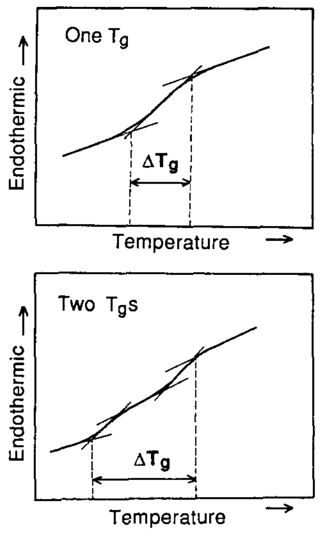

Figure 1 Definition of the breadth of the glass transition region for blends having one and two transitions

Thermal analyses were conducted in a N_2 atmosphere using a Perkin-Elmer differential scanning calorimeter (DSC-7) with heating and cooling rates of 20°C $\min^{-1}$ between 0°C and the desired upper temperature limit. In some cases, the samples were heated to a predetermined annealing temperature and held there for varying periods of time. The thermal properties reported here were obtained during a second scan. The T_g values shown were computed by the mid-point method. The breadth of the glass transition region (ΔT_g) as used here is defined in *Figure 1* where systems with both one and two glass transitions are shown. The melting temperature (T_m) was taken as the maximum of the endothermic peak. The heat of fusion (ΔH) was defined as the area integrated from 155 to 245°C and for blends this includes the melting of both species since in general it was not possible to ascertain this information individually for each component because of peak overlap.

Dynamic mechanical properties were measured by a Polymer Laboratories dynamic mechanical thermal analyser. A heating rate of 2°C $\min^{-1}$ and a frequency of 3 Hz was used for all samples. Samples for dynamic mechanical thermal analysis were moulded using an Arburg Allrounder 305-210-700 injection moulding machine at 260°C.

^{1}H nuclear magnetic resonance (n.m.r.) was used to assess the extent of interchange reaction in nylon 6/MXD6 blends. A 360 MHz Fourier transform n.m.r. spectrometer (General Electric NT-360) was used for this purpose. 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. Samples used for n.m.r. analyses were the same that had been previously run in the differential scanning calorimeter immediately following the first heat and annealing.

PHASE BEHAVIOUR OF EXTRUDED BLENDS

Melt blends of nylon 6 and MXD6 prepared at 290°C were transparent in the molten state for all compositions. On the other hand, blends prepared by extrusion at 260°C were opaque in the molten state. *Figures 2* and *3* show differential scanning calorimetry (d.s.c.) thermograms for such melt blends at the 50/50 composition and for mixtures prepared by solution methods. The melting behaviour is seen in *Figure 2* where under certain conditions nylon 6 shows dual melting points but one is

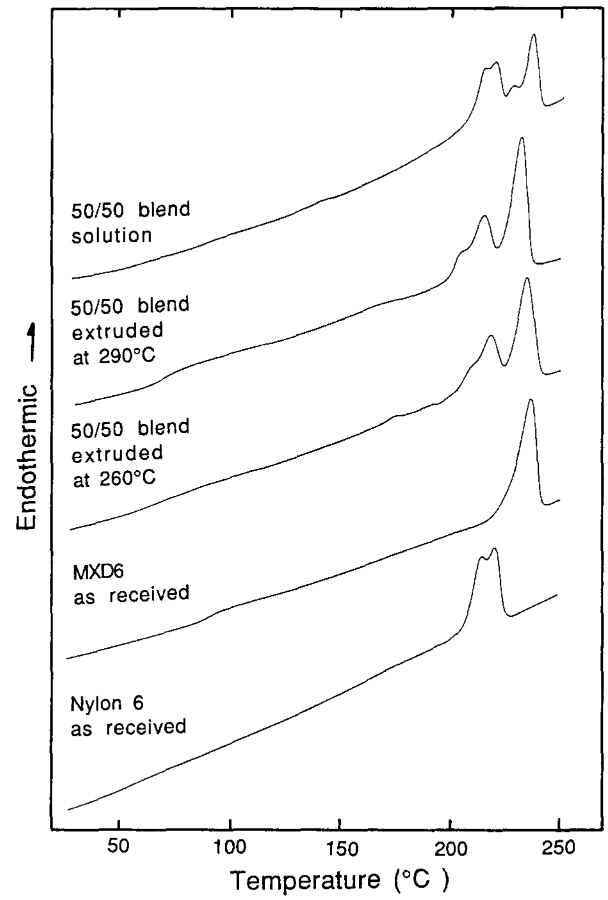

Figure 2 Sample d.s.c. thermograms showing glass transition and melting point regions

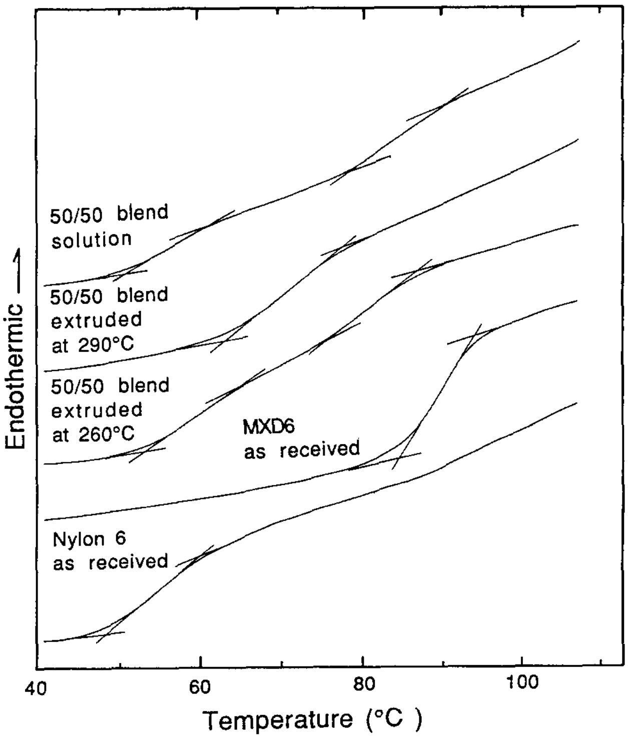

Figure 3 Sample d.s.c. thermograms expanded to show the glass transition region in detail

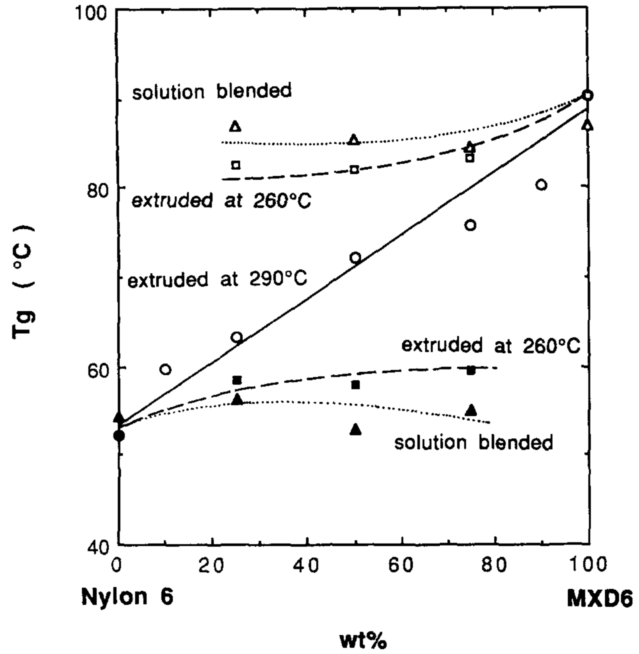

Figure 4 Glass transition temperatures from d.s.c. for nylon 6/MXD6 blends prepared in different ways

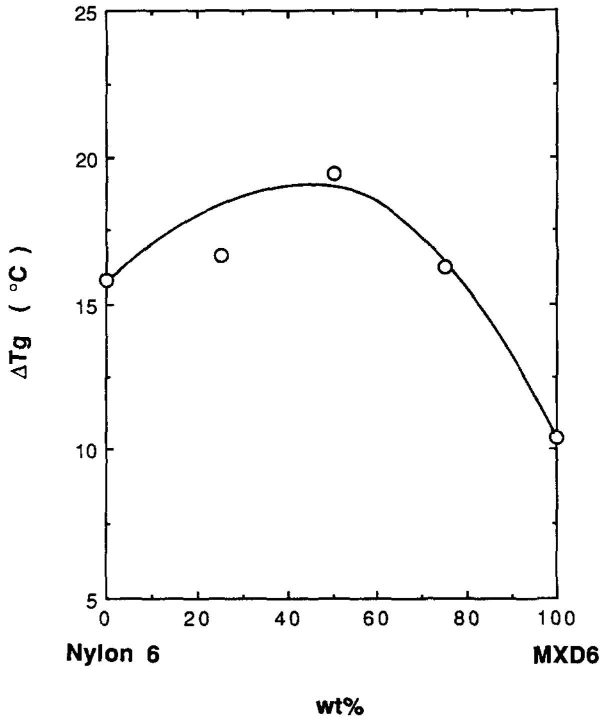

Figure 5 The breadth of the glass transition temperature region for nylon 6/MXD6 blends extruded at 290°C

dominant in all melt prepared blends. Glass transition behaviour is illustrated in *Figure 3*. The solution blend clearly shows two glass transitions; however, there is some displacement of the nylon 6 transition to higher temperature and of the MXD6 transition to lower temperature (i.e. some partial miscibility). Melt blends prepared at 260°C also show two transitions but these seem to be even more shifted than those of solution blends. When the extrusion temperature is raised to 290°C, the resulting blends have a single glass transition as seen in *Figure 3*. *Figure 4* shows these observations for other nylon 6/MXD6 compositions. *Figure 5* shows the breadth of the single T_g observed for melt blends prepared by extrusion at 290°C. Mid-composition blends have only slightly broader glass transitions than the pure components. Samples that had been melt blended at 290°C were dissolved in TFE and then precipitated into diethyl ether. The resulting materials showed one T_g. Similar experiments with blends extruded at 260°C exhibited two glass transitions. Clearly, the phase behaviour observed is dependent on prior melt processing history suggestive of irreversible interchange reaction between the nylon 6 and MXD6 rather than a reversible phase boundary [e.g. upper critical solution temperature (*UCST*) behaviour] between 260°C and 290°C.

Figure 6 shows the T_m of each component after various blending protocols. The T_m for each component is depressed relative to the pure component after solution blending but the effect is more pronounced after melt mixing, especially at the higher temperature.

Figure 7 shows the combined heat of fusion for the two components (i.e. the total endothermic peak area between 155°C and 245°C) after blending by these three methods. As may be seen in *Figure 2*, peak overlap precludes accurate resolution into the contribution from each component. The observed ΔH is below the additive line in each case, and the departure is greater for the melt blended samples. However, this departure, which is the greatest at 75% MXD6, is relatively small compared to the absolute value of ΔH.

Figures 8 and *9* show plots of $\log(\tan\delta)$ *versus* temperature for blends extruded at 260 and 290°C, respectively. For the materials prepared at 260°C, there is evidence of two glass transition peaks for the blends, whereas blends prepared at 290°C exhibit a single relaxation peak in the glass transition region.

EFFECTS OF HIGH TEMPERATURE ANNEALING

Solution blended samples of nylon 6/MXD6 blends were annealed for varying periods of time at 260, 275 and

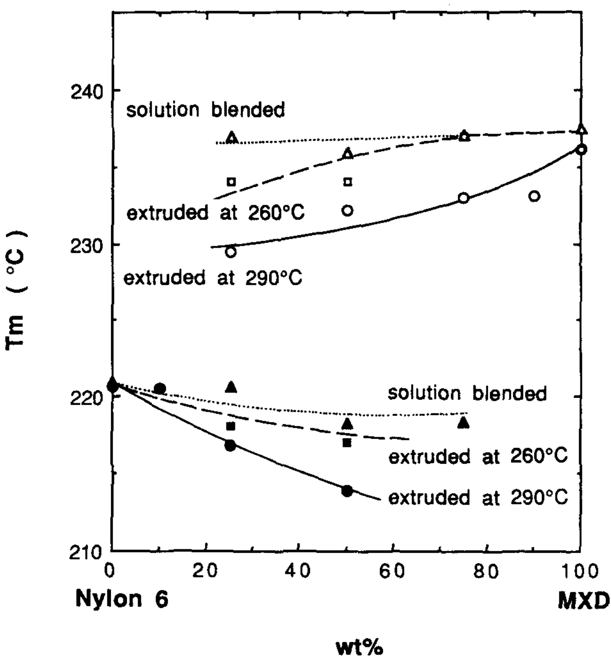

Figure 6 Melting temperature from d.s.c. for nylon 6/MXD6 blends prepared in different ways

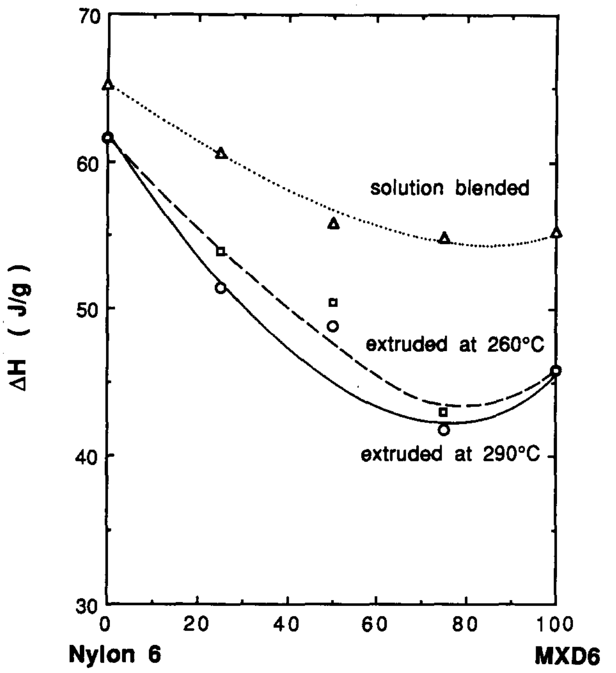

Figure 7 Total heat of fusion for nylon 6/MXD6 blends prepared in different ways

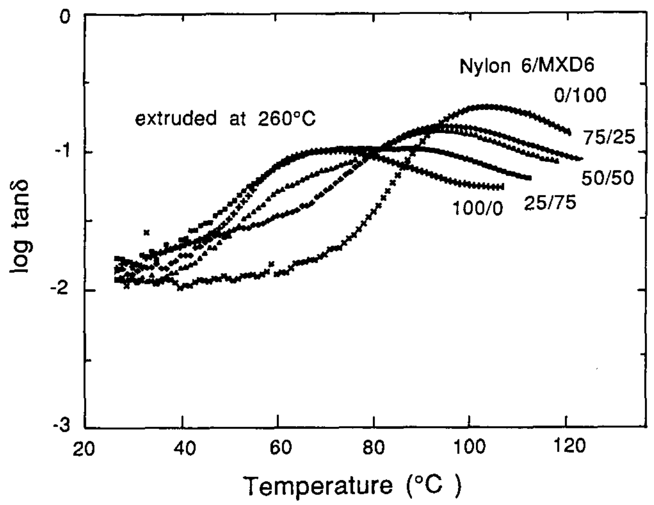

Figure 8 Log(tan δ) *versus* temperature for nylon 6/MXD6 blends extruded at 260°C

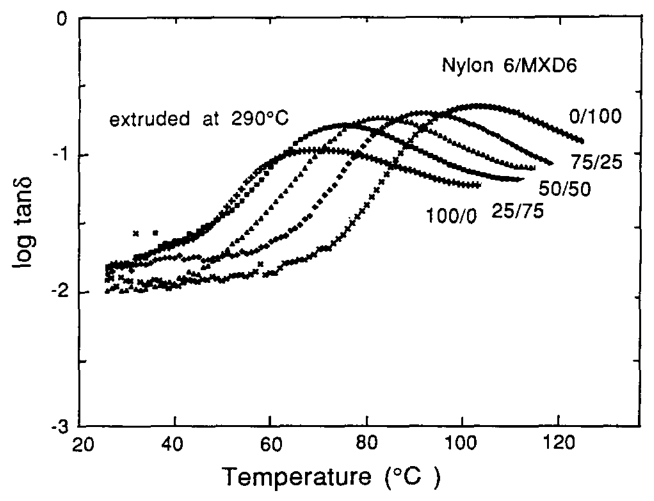

Figure 9 Log(tan δ) *versus* temperature for nylon 6/MXD6 blends extruded at 290°C

290°C. The changes observed in the thermal properties with annealing are described in the following.

Figure 10 shows how the glass transition region changes with time of annealing at 260°C. In the early stages there are two glass transitions indicative of amorphous phases that are rich in nylon 6 and MXD6, respectively. As time progresses these transitions broaden, shift towards each other and eventually merge into one broad transition (in 30 min) that narrows with further annealing time. *Figure 11* summarizes this trend for each of the three annealing temperatures used. The single T_g achieved for blends after sufficiently long annealing time continues to decrease with time in the

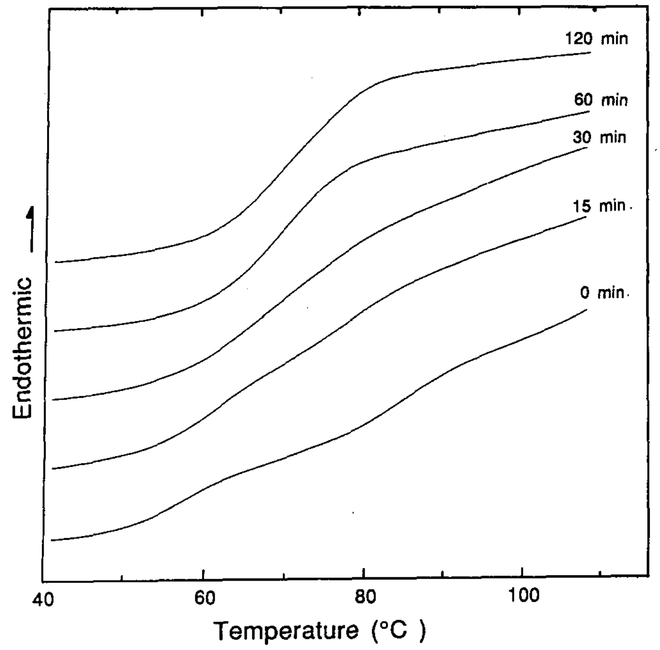

Figure 10 Temporal change of d.s.c. thermograms for nylon 6/MXD6 50/50 blends annealed at 260°C

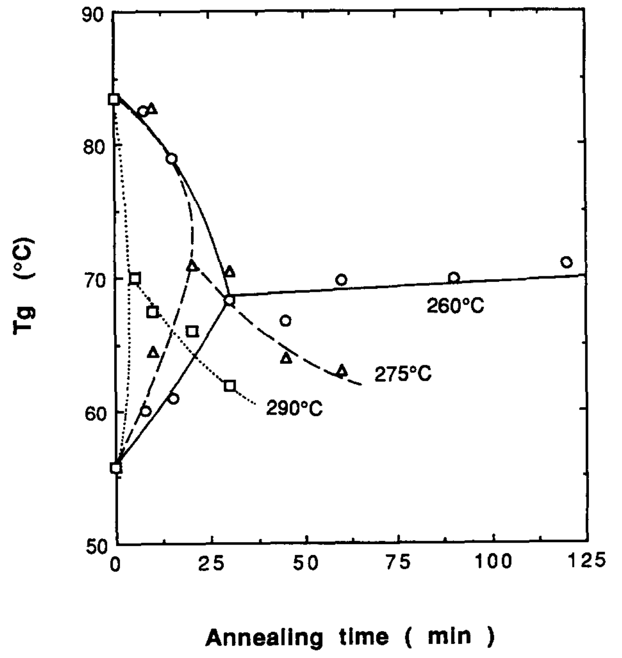

Figure 11 Temporal change of T_g behaviour of nylon 6/MXD6 50/50 blends annealed at 260, 275 and 290°C

melt at the higher temperatures. It is difficult to judge from these thermograms the points at which the two transitions merge. Therefore, a more quantitative indicator of the time for phase homogenization is given by the behaviour of the breadth of the transition region (see *Figure 1* for definition of ΔT_g) as shown in *Figure 12*. The effect of temperature on this measure of time to a certain critical reaction stage follows an Arrhenius form (*Figure 13*) with an activation energy of 130 kJ mol^{-1}. This value is comparable to the activation energy of 117 kJ mol^{-1} found for the amide exchange reaction by acidolysis using model compounds[27].

Figures 14 and *15* show that the melting points for each component and the combined heat of fusion continuously decrease with time of annealing in the melt.

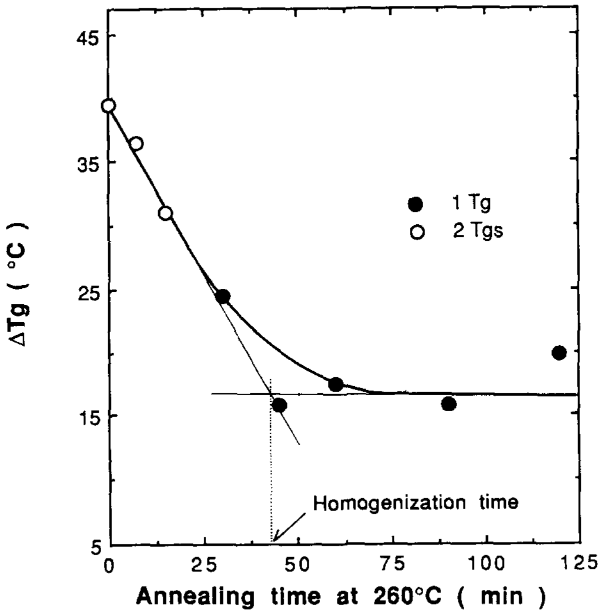

Figure 12 Determination of homogenization time as defined by the change in ΔT_g with annealing time at 260°C for nylon 6/MXD6 50/50 blends

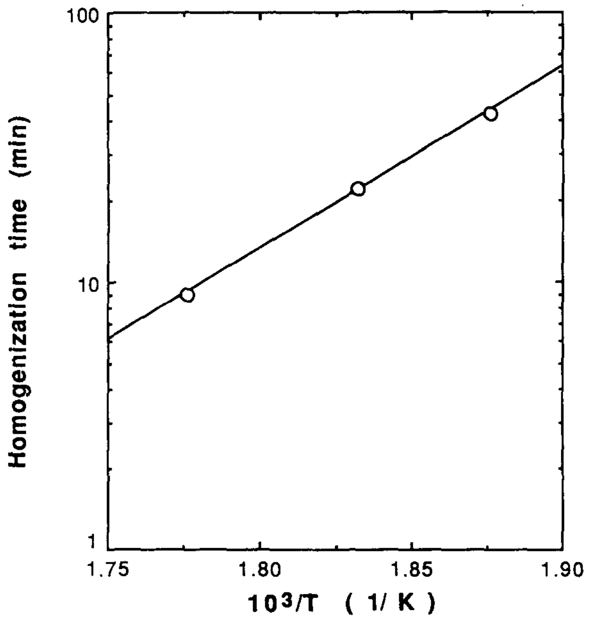

Figure 13 Arrhenius plot of homogenization time for nylon 6/MXD6 50/50 blends

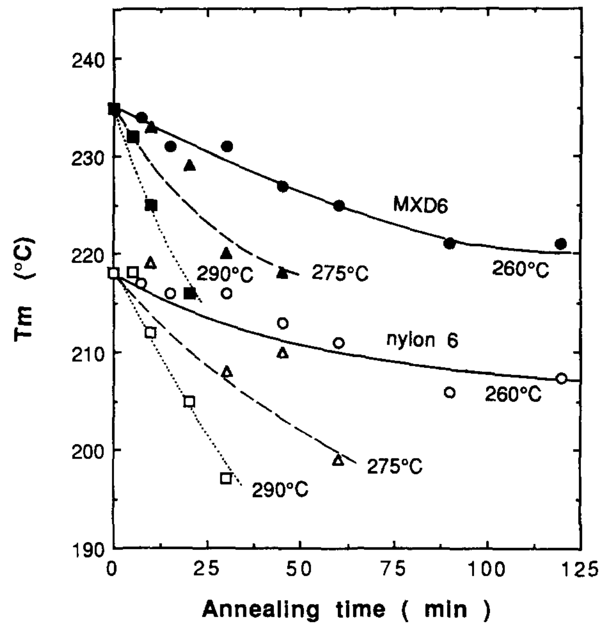

Figure 14 Temporal change of component melting temperatures for nylon 6/MXD6 50/50 blends annealed at 260, 275 and 290°C

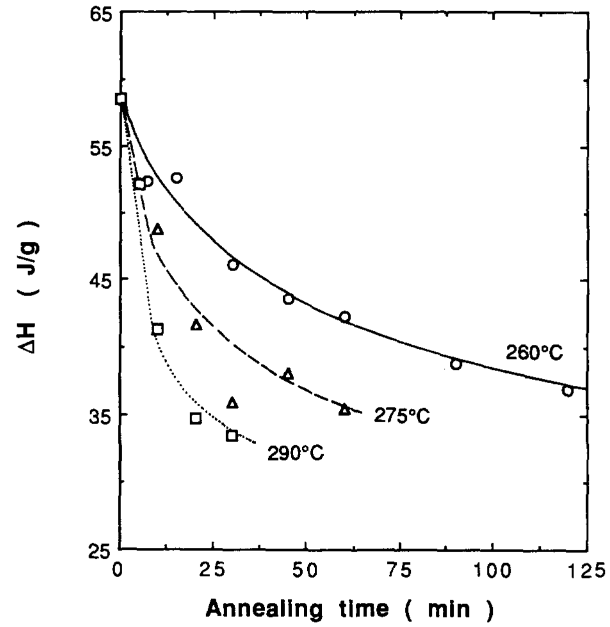

Figure 15 Temporal change of the total heat of fusion for nylon 6/MXD6 50/50 blends annealed at 260, 275 and 290°C

The rates of decline increase with annealing temperature, and there is no evidence that stable values would ever be achieved. This is rather conclusive evidence for interchange reactions that progressively lead to ever more random structures with lower T_m values and achievable levels of crystallinity.

It should be noted that static annealing experiments such as those described here are useful for following interchange reactions; however, the rate of progress to a homogeneous state may not be directly compared with the same period of time in an extruder because of the greatly increased mixing or surface area generation and renewal possible in the latter.

PROGRESS OF INTERCHANGE REACTIONS

^{1}H n.m.r. can be used to obtain more direct evidence for interchange reactions in nylon 6/MXD6 blends and their progress with time in the melt. *Figure 16* shows the ^{1}H n.m.r. spectra of the methylene groups in pure nylon 6 and pure MXD6 nylon in TFA-d. Nylon 6 is not completely soluble in TFA-d as evidenced by the turbid mixture and this results in methylene peaks that are somewhat broadened. On the other hand, MXD6 is completely soluble in TFA-d (clear solution) and the methylene peaks are relatively sharp. With the aid of other n.m.r. studies of nylon polymers[28–30], the observed peaks are assigned as shown in *Figure 16*.

Figure 17 shows the relevant n.m.r. spectra for a solution prepared 50/50 nylon 6/MXD6 blend and the evolution with time in a quiescent melt at 260°C (annealed in d.s.c.). Because of the incomplete solubility of nylon 6 in TFA-d, the solutions were somewhat turbid. However, with reaction time the solubility improved and the n.m.r. peaks become somewhat sharper. As time in the melt increases, a new peak becomes increasingly apparent at 4.60 ppm but it is somewhat overlapped with the prominent 4.68 ppm peak attributed to the methylene directly adjacent to the amine residue in MXD6.

Any changes in chemical shift are most likely for protons near the interchange reaction site. The chemical shifts for methylene groups next to the carbonyl groups

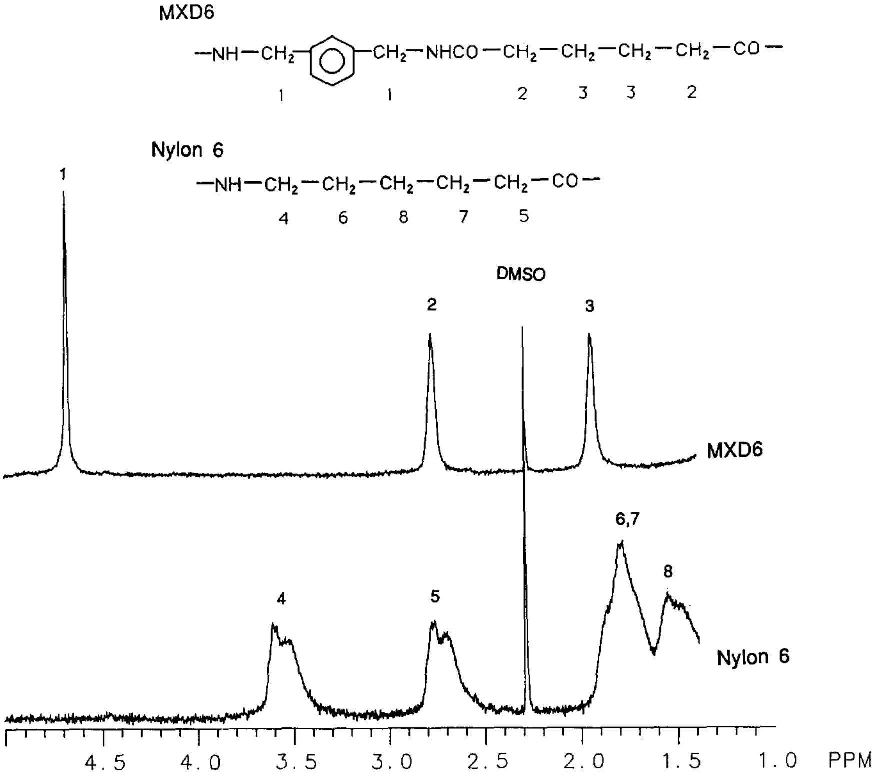

Figure 16 ^{1}H n.m.r. spectra for pure nylon 6 and pure MXD6 in TFA-d

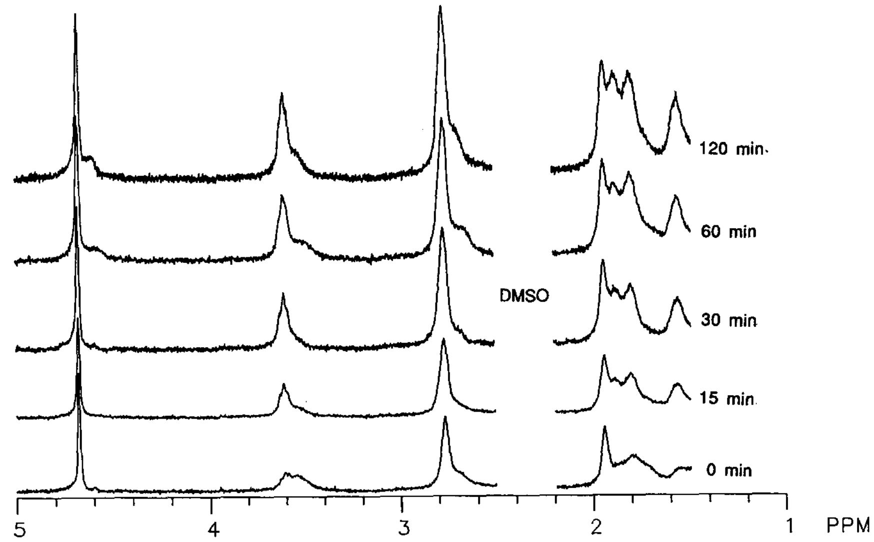

Figure 17 Temporal change of ^{1}H n.m.r. spectra for nylon 6/MXD6 50/50 blends annealed at 260°C

in nylon 6 and MXD6 are overlapped making any change here difficult to detect or analyse. The chemical shift for the methylene adjacent to the amine residue becomes sharper because of the increase in nylon 6 solubility with reaction (also true for other nylon 6 peaks); thus, intrinsic effects of chemical reaction are difficult to define from this region. Fortunately, the peak for the methylene adjacent to the amine residue in MXD6 is sharp and well-separated from all other peaks. It is well downfield from other methylenes because of the influence of the phenylene unit. However, interchange reactions at the amide linkage with nylon 6 changes the environment of this methylene unit by replacing the $(CH_2)_4$ with the longer $(CH_2)_5$ sequence. As a result, we believe that at the site of an interchange reaction there is a shift to higher magnetic field for the n.m.r. peak of the affected methylene unit. Unfortunately, the proximity of the new peak at 4.68 ppm to that at 4.60 ppm complicates the analysis but the following approximate approach seems adequate.

Figure 18 shows on an expanded scale examples in this region for pure MXD6 and a blend after a prolonged melt reaction time. For pure MXD6, the ratio of integrals

$$\alpha = y_1/x_1 \tag{1}$$

defined in *Figure 18* was found to be 2.057 indicating a slight departure from ideal peak symmetry. For this analysis, we assume that α is invariant with blending or with reaction. The extent of interchange reaction may then be assessed as the fraction the 4.60 ppm peak contributes to the total area of the two peaks using the following

$$\Psi = (y_2 - \alpha x_2)/y_2 \tag{2}$$

Figure 19 shows how this extent of interchange reaction changes with time in the quiescent melt at 260°C. Over this time interval, the reaction rate appears to be constant. The time to reach a homogeneous amorphous phase as estimated by d.s.c. at 260°C is 42 min (*Figure 10*) which from *Figure 19* corresponds to $\Psi = 0.027$. Since the average MXD6 molecule has approximately 100 repeat units with two amide groups each, it appears that only about five interchange reactions per MXD6 chain are needed to homogenize nylon 6/MXD6 blends. The n.m.r. analyses of blends that were melt extruded (*Table 1*) indicate insufficient reaction for homogenization at 260°C; however, at 290°C more than sufficient reaction, according to the above criteria, is achieved.

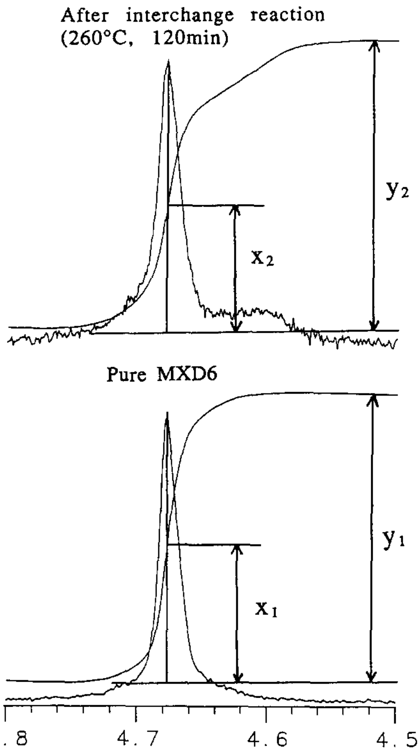

Figure 18 Calculation scheme for the extent of interchange reaction

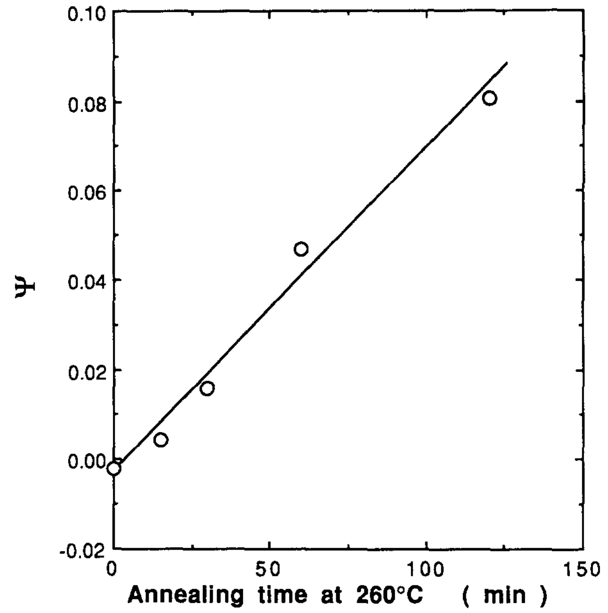

Figure 19 Extent of interchange reaction for nylon 6/MXD6 50/50 blends as a function of time at 260°C

Table 1 The n.m.r. estimates of extent of interchange reaction for melt blends

Sample	Extent of interchange reaction rate, Ψ
Melt blend at 260°C	0.007
Melt blend at 290°C	0.146
Extent of reaction required for phase homogenization	0.027

The high retention of crystallizability after phase homogenization of these blends can be understood by the fact that the resulting material is really a segmented block copolymer with sufficiently long blocks of nylon 6 and MXD6 for crystallization. The fact that phase homogenization can occur after so few interchange reactions per molecule may be understood by the following simple argument. The Flory–Huggins theory[31] predicts that a blend of two polymers A and B (each with molecular weight M and density ρ) having a positive interaction energy B will become a single homogeneous phase above *UCST* given by

$$T_c = BM/2\rho R \tag{3}$$

If a single interchange reaction occurs mid-chain as suggested in *Figure 20*, then the theory of Leibler[32] suggests that this block copolymer of total molecular weight M will become homogeneous when heated above the critical temperature

$$T_c = BM/10.5\rho R \tag{4}$$

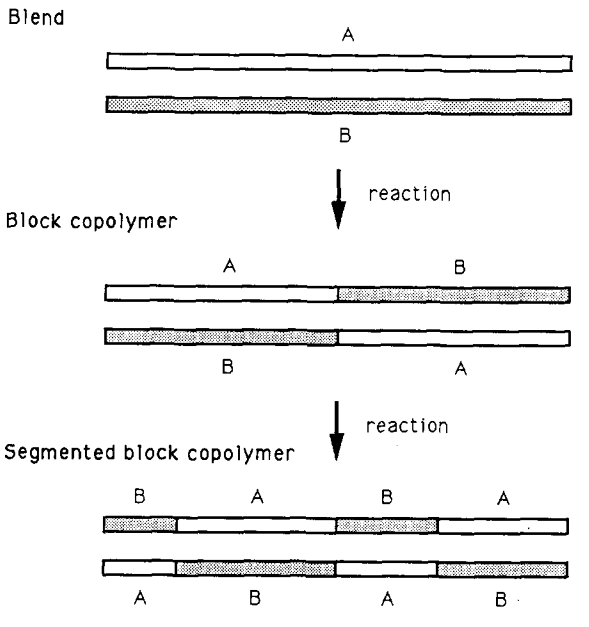

Figure 20 Illustration of the progressive change in molecular structure caused by interchange reactions

Thus, the block copolymer becomes homogeneous at an absolute temperature which is 1/5.25 that at which the unreacted blend does. While such theoretical calculations are not yet available, it is clear that multiple interchange reactions will lower the temperature for phase homogenization even further. From this simple model we can see that nearly miscible (positive but small *B*) blends will require fewer reactions to reach phase homogenization within processing and use temperature ranges than a more strongly immiscible pair (large positive *B*). Furthermore, the small amount of partial miscibility that may accompany a weak interaction may facilitate the interchange reaction by allowing the two types of chains more access to each other for reaction.

CONCLUSIONS

Melt blends of the partially aromatic polyamide MXD6 with nylon 6 were found to be either heterogeneous (two amorphous phases) or homogeneous (one amorphous phase), as shown by glass transition behaviour, depending on processing temperature. Thermal annealing of mixtures that were originally heterogeneous caused the eventual formation of homogeneous blends. Various physical observations combined with ^{1}H n.m.r. studies provide convincing evidence that the observed phase homogenization is the result of interchange reactions between the two polyamides which are not fully miscible with each other prior to any reaction. The n.m.r. studies suggest that phase homogenization occurs after as few as five interchange reactions per polymer chain. Thus, the reacted product is a segmented block copolymer rather than a random copolymer. This is consistent with the fact that the homogeneous melt blends prepared by extrusion at 290°C retain rather high levels of crystallinity and, thus, stiffness and strength.

Phase homogenization can be achieved by relatively few interchange reactions when the physical interaction energy between the two starting materials is relatively small, i.e. near miscibility, as shown here using thermodynamic arguments for phase behaviour of blends and for block copolymers. Using the recent work by Ellis[1] on the phase behaviour of physical blends of aromatic and aliphatic polyamides, one can estimate that mixtures of MXD6 and nylon 6 might be nearly miscible or have a low interaction energy density. Systems of this type permit development of unique materials that combine the properties of the two parent materials in the same way as if they were miscible, i.e. amorphous phase homogeneity and high levels of crystallinity. For blend components far from miscibility, the extent of interchange reaction would have to approach a structure similar to a random copolymer before phase homogenization would occur. Such materials would suffer severe losses in crystallinity and the attendant sacrifices in properties.

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