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Miscibility of Polyamide Blends. 2. Thermal Study of Poly(hexamethylene isophthalamide)/Nylon-*n*,*m* Blends

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ABSTRACT: Miscibility of a series of nylons-6,*m* with poly(hexamethylene isophthalamide), abbreviated 6I nylon, was investigated. Four polyamides (nylon-6,5, nylon-6,7, nylon-6,8, and nylon-6,9) were found miscible, on a DSC scale, with 6I nylon. A series of nylon-*n*,*m* which had the same number of CH_2 groups as nylon-6,7 was also studied; no miscible blend with 6I nylon was found. This was taken as direct evidence of the importance of average interamide distances for miscibility. Negative deviations from linearity in T_g–composition behavior of the blend are proposed to stem from conformational changes leading to weaker van der Waals interactions. These weak interactions are counterbalanced, in terms of energy, either by more ordered hydrogen bond networks or by entropy effects. For nylon-6,8/6I nylon blend, an S-shaped curve was observed, which is attributed to the occurrence of variations of chain morphologies with blend composition.

Introduction

It is generally accepted that polymer miscibility results mostly from favorable interchain interaction formation. These can be weak, van der Waals forces, or stronger forces such as charge transfer and hydrogen bonds. It was initially proposed that, for polymers which strongly self-associate, like polyamides, miscibility would be improbable because of the energetic cost of breaking strong interactions in order to form the blend.[1] Many such miscible systems are now known (see, for example, refs 2–7). How favorable interactions form in these systems, whether they can be predicted or modeled, and what is the effect on thermal behavior are however still open to debate.

Interchain interactions which occur in miscible blends are responsible for the observed macroscopic properties. These, in turn, are often used to determine miscibility. The glass transition temperature T_g, as measured by DSC, falls into this category and is probably the most widely used miscibility criterion, although limited to investigation of domains approximately larger than 10 nm.[8]

In the first article of this series,[7] blends of poly(*n*-methylene isophthalamides), or *n*I nylons, with poly(*m*-phenyleneisophthalamide), abbreviated mpI, were studied. All showed similar negative deviations in the T_g–composition curves. It was noted that the ratio of hydrogen bonding atoms vs the total number of atoms in the repeat unit (excluding hydrogen atoms) remained fairly constant. The usefulness of this observation as a rule of thumb for predicting possible miscible blends was pointed out. A binary interaction model previously used for polyamides[6] was also tested, but fit with experimental results was poor. Although it was proposed that this was related to the inability of this model to take into account possible hydrogen bond formation for homopolyamide blends, other factors, such as slightly incorrect prediction parameters, could not be excluded. Furthermore, the high rigidity of mpI could not be taken into account by this model and was also a possible cause of discrepancy.

In the present article, 6I nylon has been blended with more flexible chains, namely, nylons-*n*,*m*. Variations in chain length and distribution of aliphatic segments allowed changes not only in composition but also in relative interamide distances. The present system allowed evaluation of these factors which may affect interchain interaction formation, and in particular hydrogen bond formation. Consequently, these factors are liable to affect the miscibility of strongly interacting polymers.

Furthermore, these blends show changes in thermal behavior when varying the chain length. Various theories accounting for T_g–composition relationships in miscible blends are found in the literature. Most take into account, either directly or indirectly, interaction formation and can therefore be used to provide an insight on interaction formation in the blends. Perhaps the most widely used is the Gordon–Taylor relationship.[9,10] Derivations from the Gordon–Taylor relationship[11,12] and an alternate theory proposed by Brekner, Schneider, and Cantow[13] have been proposed to take into account specific interactions. Their application to the present system will be attempted.

For these reasons, the 6I nylon/nylon-*n*,*m* blends constitute a choice system for comparing existing theories relating T_g to interactions. It is hoped, using this system, to arrive to a better understanding of the relationship between macroscopic properties and interaction formation at the molecular level for the systems forming strong hydrogen bonds. The present system is especially well suited for the investigation of the relationship between miscibility, interchain interaction formation, and average interamide distances.

Experimental Section

Synthesis and Characterization of the Homopolymers. Polymers used in this study were synthesized by interfacial polycondensation following the procedure of Beaman and co-workers.[14] Molecular weights were estimated through viscosity measurements performed at 25 °C in *m*-cresol for nylons-*n*,*m* and in concentrated sulfuric acid for 6I nylon using a Ubbelohde viscosimeter and are reported in Table 1. The Mark–Houwink parameters of nylon-6,6, published by Elias and Schumacher,[15] were used for all nylons-*n*,*m* ($K = 3.53 \times 10^{-2}$ mL g^{-1}, $a = 0.792$). It must be noted

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Table 1. Molecular Weights of the Polymers Used in This Study

polymer	$[\eta]$ (mL g^{-1})	$10^{-4} M_v$
nylon-6,3	20.0	0.30
nylon-6,4	69.0	1.4
nylon-6,5	102	2.4
nylon-6,6	85.0	1.9
nylon-6,7	115	2.8
nylon-6,8	121	2.9
nylon-6,9	145	3.7
nylon-6,10	75.0	1.6
nylon-3,10	58.4	1.17
nylon-4,9	55.4	1.10
nylon-5,8	82.2	1.80
nylon-7,6	71.1	1.50
nylon-8,5	62.7	1.28
nylon-9,4	14.1	0.19
6I nylon	61.0	1.00

that this approximation is expected to induce an error which will grow as the chain lengths of the nylons deviate from those of nylon-6,6. Therefore, the molecular weights determined by this method are only indicative. For 6I nylon, the Mark–Houwink parameters reported by Neilinger and co-workers were used ($K = 3.24 \times 10^{-2}$ mL g^{-1}, $a = 0.78$).[16]

Preparation and Characterization of the Blends. Nylon-6,*m*/6I nylon blends were prepared by solvent casting in trifluoroacetic acid (CF_3COOH). Solutions of 100 mg of polymer in approximately 1 mL of trifluoroacetic acid were prepared and poured into Petri dishes. These were placed in a desiccator to allow slow evaporation in the absence of humidity. Once a solid film was formed, the Petri dishes were transferred to a vacuum oven where the samples were thoroughly dried under dynamic vacuum at 140 °C to remove all traces of solvent. DSC scans were performed on the pure polymers to verify whether the T_g had varied, in which case the samples were dried further. Total drying time was approximately 1 month. Nylon-*n*,*m*/6I nylon blends were prepared both by solvent casting and by precipitation in water of a concentrated sulfuric acid solution. In the precipitation method, a solution containing 100 mg of polymer in approximately 2 mL of concentrated sulfuric acid was added to 100 mL of water. The polymer precipitated, and the acidic solution was decanted out. The polymer was rinsed thoroughly with water until neutrality of the washing water was reached. Samples were then placed in a desiccator and allowed to dry several days. They were then transferred to a vacuum oven where they were further dried as described for the solvent casting method. In all cases, blends containing approximately 10, 25, 50, 75, and 90% w/w 6I nylon were investigated.

Thermal analysis was performed at a heating rate of 20 °C/min using a Perkin-Elmer Series 7 differential scanning calorimeter (DSC) calibrated for temperature with indium. A baseline was registered at regular intervals by putting an empty cell on the head, and it was subtracted from the measured data in all cases. Measurements of glass transition temperatures (T_g) are reported as the midpoint value. Depending on the width of the transition, the error associated with the T_g varied. This has been taken into account when determining the error bars reported in the figures. At least two successive scans were registered, since on the first one, as often is the case in DSC, the T_g was usually not observable. This was attributed to a poor polymer–cell contact during the first run. Samples were cooled as fast as possible between the two runs to limit thermal degradation. Since this procedure induced changes in thermal history of the samples, and therefore in crystallinity, the latter was estimated only after the last DSC scan and on the same sample that was used for DSC. Since most scans had to be started under room temperature, cooling was performed in all cases using liquid nitrogen.

Care has been taken not to reach the decomposition temperature of the nylon-*n*,*m* which is around 200 °C, except when melting of the blend was deliberately sought. In such cases, melting was performed at 225 °C during a very short time (2 min) to minimize decomposition, cross-linking, and transamidation reactions and rapidly cooled immediately after in the DSC apparatus. Some thermal degradation inevitably occurred, but the procedure described was used to keep it at a minimum. Indeed, after DSC measurements, the cells were opened for X-ray measurements. All samples had taken a brownish tint. For those having been melted, the discoloration was more intense, which was evidence of a more pronounced thermal degradation.

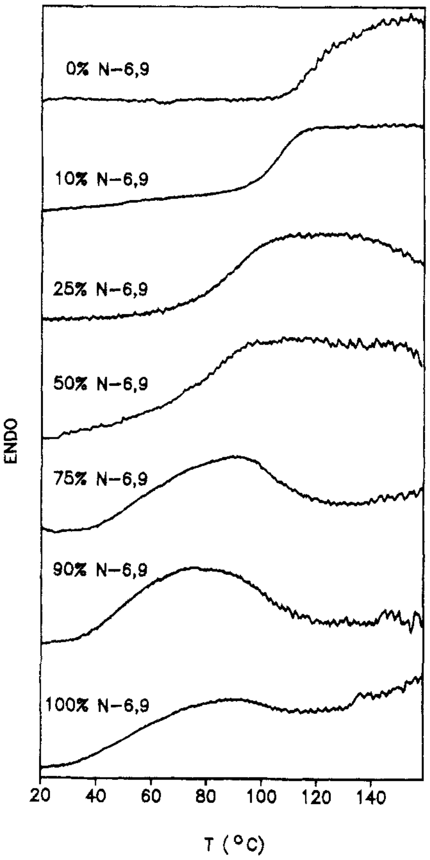

Figure 1. Thermograms of nylon-6,9/6I nylon blends.

Analysis of the phase behavior has been achieved according to two criteria: the presence of only one T_g at an intermediate value between those of the two pure homopolymers was the criterion for miscibility, and the presence of two transitions near the T_g of each pure polymer that for immiscibility. A representative series of DSC curves, those of nylon-6,9/6I nylon blends, is reported in Figure 1. In general, the width of the glass transition remained fairly constant. In some instances, a relaxation occurred after the transition and is attributed to thermal treatments, which could be heating during the first DSC scan or, when specified, the short melting necessary to check for possible solvent-induced phase separation.

X-ray scattering was used to determine the crystallinity of the blends. X-ray diffraction spectra of the samples were taken after DSC measurements for $2\theta = 5-60°$ with the Cu Kα, graphite-monochromatized radiation on a Rigaku RU200B rotating-anode generator at 195 kV and 55 mA and a scintillation counter. Crystallinity determination was done according to the method of Ruland[17] modified by Vonk, using the program FFCRYST.[18] The 6I nylon spectrum was used as the reference amorphous spectrum for all samples. Amorphous intervals used for the scaling procedure were adjusted for each different polymer to exclude the characteristic crystalline peaks from the amorphous intensity calculation. The crystallinity X_c, total nylon-*n*,*m* weight fractions x, and corrected amorphous nylon-*n*,*m* weight fractions x_a are given in Table 2. Crystallinity was calculated from diffraction spectra taken after the last thermal treatment to get a correction which matched as accurately as possible the measured DSC scan. However, the thermal history of the samples varied greatly before and after DSC scans, and in some cases, melting was

Table 2. Total Weight Fraction x and Amorphous Weight Fraction x_a after Crystallinity Correction of Blends Showing the Reported T_g

blend	x (±0.0005)	% cryst (±5)	x_a (±0.04)	T_g (°C) (±4)
6,5/6I	0.1020	0	0.10	111
	0.2658	0	0.27	92
	0.4985	18	0.39	80
	0.7505	33	0.63	72
	0.9012	38	0.84	45
6,7/6I	0.103	0	0.10	80
	0.247	7	0.19	70
	0.499	15	0.41	47
	0.750	27	0.66	35
	0.897	16	0.88	41
6,8/6I	0.104	0	0.10	108
	0.245	10	0.16	95
	0.499	30	0.28	90
	0.746	31	0.63	87
	0.888	37	0.82	83
6,9/6I	0.1022	0	0.10	105
	0.2485	5	0.21	89
	0.5045	37	0.21	81
	0.7488	45	0.54	58
	0.9010	51	0.80	50

also performed. The reported values should therefore not be taken as indicative of the relative crystallinities of the blends but only as representative of the composition which gave rise to a particular T_g. Since no melting was applied to the pure polymers, these show a lower crystallinity than some blends. In all cases, 6I nylon remained completely amorphous and nylons-*n*,*m* crystallized partially. Representative X-ray diffraction spectra of blends with different nylon-6,*n* chain parity, namely, nylon-6,8 and nylon-6,9 are represented in Figure 2.

Results and Discussion

Miscibility of the Nylon-6,*m*/6I Nylon Blends. A first series of blends, nylons-6,*m* with 6I nylon, were studied for $m = 3-10$. Only nylon-6,7 and nylon-6,8 were found to be miscible with 6I nylon in the whole range of compositions.

Nylon-6,5 blends showed partial miscibility in the range of high nylon-6,5 composition ($x \geq 50\%$ w/w). Because of the acute thermal degradation of nylon-6,I around the melting point of nylon-6,6, blends had to be prepared via solution evaporation or reprecipitation. Although the chosen solvents showed a very high affinity for both polymers of the blends, it was not possible to exclude completely the possibility of having precipitated one of the polymers before the other. This would induce a phase-separated system in spite of the fact that the equilibrium state would be a miscible blend. To verify if this had occurred, the blends which had been found immiscible were melted to let the system approach its equilibrium state. As mentioned in the Experimental Section, a rapid melting was performed to limit decomposition and transamidation reactions, since these could also influence the observed miscibility. Transamidation reactions are known to result in crosslinking,[19] and miscibility of copolymers would then be determined instead of that of the homopolymers. Crosslinking can lead to a homogeneous, copolymeric phase, although it has been reported to induce phase separation in PEO/epoxy resins blends.[20] Melting extended the miscibility range to two more blends: nylon-6,5 and nylon-6,9 were added to the list of polyamides miscible with 6I nylon. Whether the enhancement of miscibility was due to transamidation or reflected the equilibrium state of the system is difficult to assess. However, such a short melting time should result only in limited transamidation, so that blends must have been very close to the requirements for miscibility in the first place. We therefore concluded that, within experimental error of the technique used here, both the nylon-6,5 and the nylon-6,9 were miscible with nylon-6,I.

A gap can be noted along the miscibility range: nylon-6,6 was not found miscible with 6I nylon, even after melting. This observation is in contradiction with those of Ellis[21] and Zimmerman and co-workers,[2] who previously reported miscibility of these two polymers. The most probable cause of discrepancy between these studies and the present report lies in the blend preparation method: in the work of Zimmerman and co-workers, melt blending was used in conditions in which transamidation was likely to happen. In the work of Ellis, a coprecipitation from solution was performed for a single blend with a 50:50 composition. It is not known whether the observed difference in miscibility in this particular case stems from variations in the polymer (polydispersity, molecular weight, nature of end groups, presence of stabilizers, etc.) or from preparation conditions.

For polyamides, the preparation method is a delicate issue. Both polyamides, the preparation method is a delicate issue. Both precipitation and solvent evaporation methods could result in nonequilibrium phases, whereas melt blending is likely to result in copolymer formation. In the present work, solution evaporation from trifluoroacetic acid was preferred over precipitation methods because resulting films were suitable for FTIR investigation, which will be the subject of a future article. The solubility of both polymers in this solvent is excellent, which minimizes possibilities of preferential precipitation of one of the components of the blend. Results from this method were compared for the nylon-*n*,*m* with 11 CH_2 groups with a coprecipitation method from H_2SO_4 solution into water, and both gave similar results. Furthermore, since various concentrations were used, the probability of accidental phase separation for all concentrations is very limited. It is therefore concluded that the nylon-6,6 used in this study is immiscible with 6I nylon but that this is probably a borderline case, for which small variations in the polymer synthesis or blend preparation could lead to variations of polydispersity and molecular weight and consequently to different miscibility behavior.

Influence of Chain Length Variation. One of the aims of this work was to investigate the influence of relative chain length on miscibility. In the first paper of this series, it was proposed that fluctuations of the average distance between consecutive amide groups along a polymer chain affected miscibility of homopolyamides. Strictly speaking, to verify this hypothesis, completely rigid systems would be preferable, but these would have very little probability of forming the interactions necessary for miscibility. Instead, in the present study, the relative number of CH_2 groups in aliphatic chains were changed. In this way, the average interamide distances are varied. The maximum interamide distances are easy to evaluate, since these pertain to an all-trans extended conformation of the chain. On the other hand, evaluation of the average interamide distance is a much more complicated problem, since these depend on the arrangement of the aliphatic chains in the amorphous phase. It has therefore not been attempted here. However, varying the number of CH_2 segments in each aliphatic chain while maintaining the chemical composition of the repeat unit constant will directly affect this value. We therefore have a qualita-

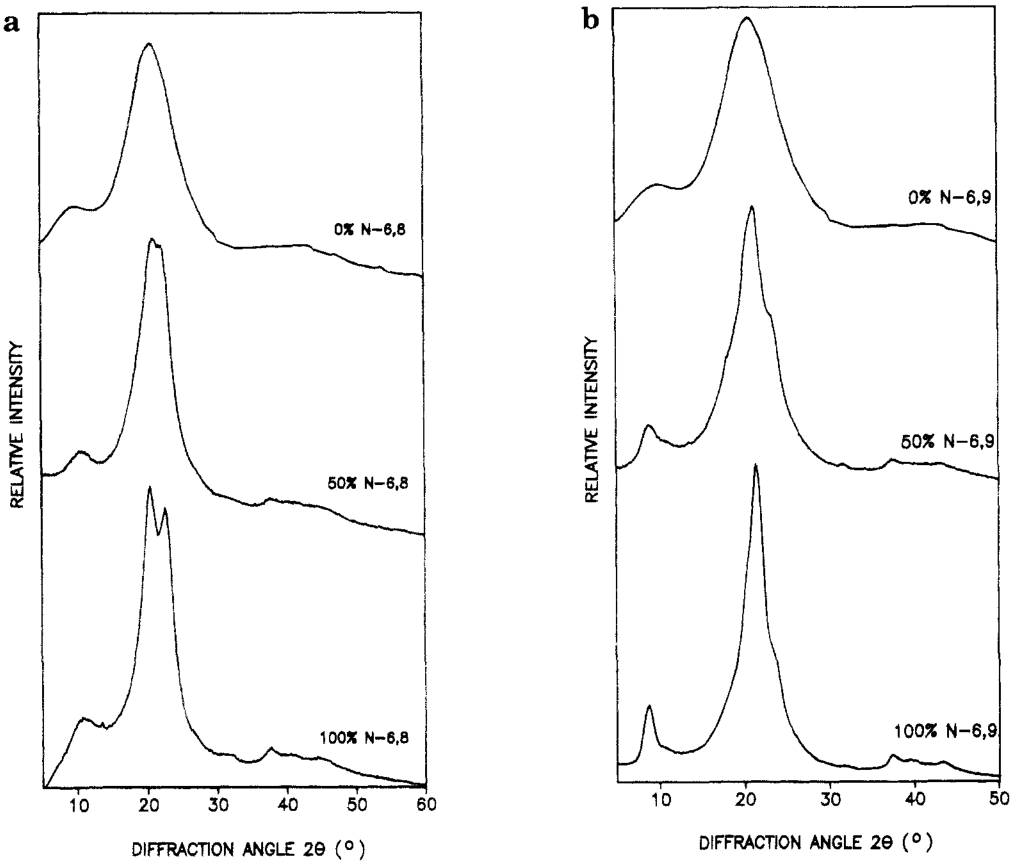

Figure 2. X-ray diffraction spectra of pure polymers and 50% w/w blends: (a) nylon-6,8/6I nylon blends; (b) nylon-6,9/6I nylon blends.

tive means of evaluation of this effect with the present system.

One of the miscible blends, the nylon-6,7/6I nylon blend, was used as a starting point. Nylons-*n*,*m* with the same number of CH_2 groups as nylon-6,7 were synthesized for $n = 3$ and $m = 10$ to $n = 9$ and $m = 4$, and blends with 6I nylon were prepared. All, apart from the initial miscible blend, were found to be completely immiscible at all studied compositions. Melting did not alter this behavior. It is quite significant that a variation of one CH_2 unit from one of the aliphatic segment of nylons-*n*,*m* to the other (nylon-7,6 instead of nylon-6,7) affected drastically the miscibility. This is interpreted as being a direct indication of the importance of the interamide distance in the miscibility behavior of homopolyamides.

Miscibility Prediction. Methods of predicting miscibility have attracted much attention. The solubility parameter approach has not been found useful for hydrogen bond forming polymers. The group of Painter and Coleman has devised a prediction method, which is however at the moment limited to systems where either no hydrogen bonds occur or where hydrogen bonds are formed between an acceptor–donor and an acceptor.[22]

As mentioned previously, Ellis has proposed the use of the binary interaction model for prediction of miscibility of polyamide blends.[6] This model is derived from the Flory–Huggins equation of state theory, using the assumption that polymers are composed of groups for which interaction parameters can be calculated and are additive, thus allowing calculation of the interaction parameter of a blend. However, as mentioned previously, discrepancies were found between predictions using this model and miscibility of *n*I nylons with mpI.[7]

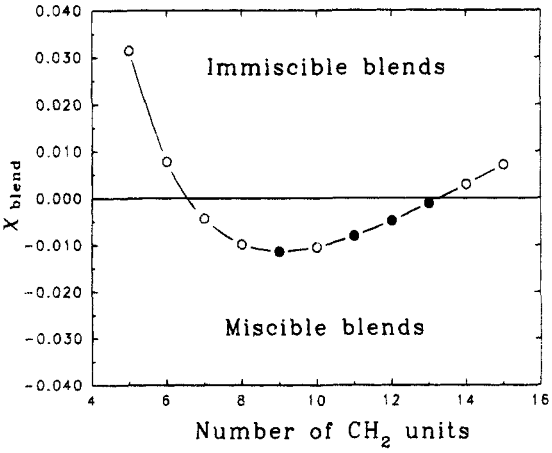

Figure 3. Predictions of χ_{blend} as a function of total number of CH_2 units in nylon-*n*,*m* using the binary interaction model (empty circles, blends experimentally found immiscible; filled circles, blends found miscible in the present study).

Various reasons were invoked for these discrepancies, among which was the imprecision of the χ group parameters used to calculate the total interaction parameter of the blends, which were the same for the interaction of para- and meta-substituted aromatic moieties.

Predictions of χ_{blend} using the binary interaction model are reported in Figure 3 as a function of the total number of CH_2 units in nylons-*n*,*m*. The blends which have been found miscible in the present work are represented by dark circles. For the 6I nylon/nylon-*n*,*m* blends, a maximum miscibility is predicted for 9 CH_2 units, with a miscibility window ranging from 7 to 13. The experimental maximum miscibility is shifted with respect to the predictions: Experimental data showed miscibility only for 11 and 12 CH_2 units (nylon-6,7 and nylon-6,8). Sample melting extended the miscibility to 9 and 13 CH_2 units (nylon-6,5 and nylon-6,9), but the miscibility range remains more limited than the predicted one. These deviations could be due to slightly incorrect χ parameters of the individual chemical groups that make up the repeat unit, since these were derived from blends comprising *trans*-substituted aromatic moieties. Correct χ parameters could not lead to a miscibility gap such as the one observed for nylon-6,6. However, the observed immiscibility of the nylon-6,6/6I nylon blend is in contradiction with previous reports, as stated earlier, and believed to be a borderline case. Nevertheless, incorrect χ parameters are also insufficient to justify the observation that nylons-*n*,*m* with 11 CH_2 units do not all exhibit the same miscibility behavior with 6I nylon. Since these all have the same composition, their miscibility behavior should be identical according to the binary interaction model, as proposed for nylons by Ellis.[6]

Another possible cause for discrepancy is that this model does not take into account the possibility, on a molecular level, for the blended polymers to form hydrogen bonds. This is proposed to be related to the average interamide distances, which should match in the amorphous phase if hydrogen bond formation is to be possible. As stated earlier, no quantitative evaluation of this factor was attempted here. Instead, variations of the distribution of CH_2 groups between the two aliphatic chains of the repeat unit was taken as a qualitative means of investigating this factor.

It has previously been stressed that a good match of these average interamide distances was not sufficient for miscibility and that the energy involved in the interacting chains should also be reasonable; otherwise the hydrogen bonds could not form.[7] The assumption that hydrogen bonds will form if other interactions between segments are favorable completely neglects geometrical limitations to the formation of such bonds. Interamide distance is one of the factors involved in these limitations. Neglecting these geometrical limitations may be valid for random copolymers, for which geometry and, therefore, interamide distances vary almost statistically. However, for homopolymers, interamide distance variations, although still fluctuating, are limited to a much smaller range since they are related only to changes in chain conformation. For this reason, it was previously proposed that this assumption is too drastic for regular homopolymers.

The first system studied, composed of rigid and semirigid chains (poly(*m*-phenylene isophthalamide) and *n*I nylon blends), showed that miscibility was much more restricted than that predicted by the binary interaction model. The systems studied here were chosen as a test for more flexible chains, and indeed predictions using the binary interaction model match better, but still not adequately, the observed behavior. This model has however been used intensively on copolymers, including systems of copolyamides with homopolyamides, and appears to give very good results in these cases. It is concluded that, for homopolymers, the binary interaction model can be used for screening purposes, but shows limitations as great as those of the rule of thumb proposed in the first article of this series.

This rule of thumb was proposed as a screening method: For miscibility to occur, the balance between hydrogen-bonding and non-hydrogen-bonding atoms should be kept approximately constant. In other words, a six-carbon aromatic ring should be replaced by an aliphatic chain of approximately 6 atoms for miscibility to be possible. Using this approach, it is easy to explain the immiscibility of 6I nylon with nylon-*n*,*m* when both *n* and *m* are very different from 6. Other factors affecting hydrogen bond formation will however obviously affect miscibility. Nylon-6,*m*/6I nylon blends miscible before melting have an aliphatic chain containing 5 and 6 carbon atoms (nylon-6,7 and nylon-6,8 respectively), which agrees well with the proposed rule. After a brief melting, two more miscible blends were found, those with 3 and 7 carbon atom chains (nylon-6,5 and nylon-6,9), giving a poorer fit. Furthermore, nylon-6,6 is not miscible with 6I nylon or is at best at a miscibility edge, whereas it contains a 4 carbon atom chain and should therefore show a higher miscibility than that of nylon-6,5. The present study therefore highlights the limitations of this rule of thumb, while at the same time confirming its usefulness for screening purposes.

Dependence of T_g on Composition. The glass transition temperature, T_g, is often used as an indicator of miscibility. Information gained through T_g has been proposed to be related to interactions present in the blends. To use the T_g behavior in this respect, it is necessary to correct the bulk compositions, since a part of the chains can segregate into crystalline domains formed of one pure polymer. The bulk composition, in these cases, is therefore not equivalent to the composition of the amorphous phase. Although 6I nylon is amorphous in the conditions used here, nylons-*n*,*m* are highly crystalline, and the crystals retain their identity in the blends. The overall composition x of a blend does not, therefore, correspond to the composition x_a of the amorphous phase.

Many methods can be used to quantify crystallinity. They are however more difficult to use on blends. For instance, density mesaurements would require the knowledge of the density of the pure amorphous phase, which is bound to change with composition if free volume varies. Vibration band overlaps preclude the use of FTIR. DSC is normally appropriate if one knows the pure polymer melt enthalpies of the crystalline phase, which is not the case for blends studied here. Furthermore, severe polymer degradation is observed at the melt temperature. For these reasons, X-ray diffraction was preferred. One approximation was made: the scattering of the amorphous phase was supposed independent of composition and equal to that of 6I nylon. This seems justified in view of the published spectra of amorphous nylon-6,6,[23] which is almost superimposable with that of 6I nylon. Although this approximation may be a source of error, it is expected to be much less severe than that related to degradation of the samples in DSC. Total weight fractions x and corrected amorphous weight fractions x_a are given in Table 2. The latter have been used throughout T_g–composition studies, unless otherwise specified.

One of the most widely used criteria for miscibility determination, and indeed the one used in the present work, is that of T_g variation with composition. At T_g, the thermal energy necessary to break part of the interchain interactions is reached, and emergence of segmental mobility results. The nature of these movements is not fully understood: what is the size of the chain section that undergoes movements? What is the effect of the overall conformations of neighboring chains?

In the case of polyamides, these questions are crucial for the understanding of T_g–composition behavior.

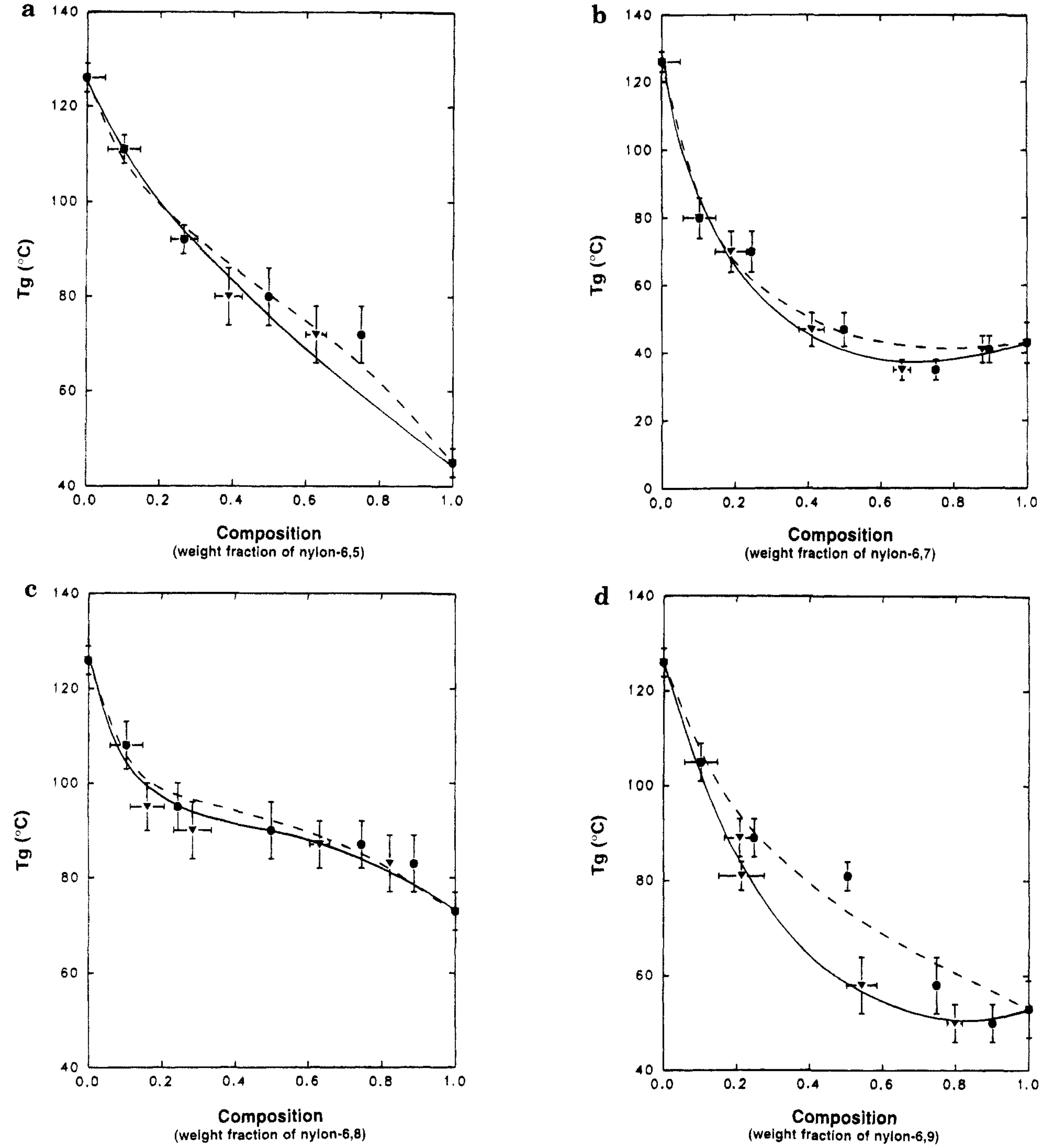

Figure 4. Glass transition temperature changes with respect to composition before (circles) and after (triangles) crystallinity correction: (a) nylon-6,5/6I nylon blend; (b) nylon-6,7/6I nylon blend; (c) nylon-6,8/6I nylon blend; (d) nylon-6,9/6I nylon blend.

Although van der Waals interactions are undoubtedly severely disrupted at T_g, thus allowing large-amplitude movements of the chains, hydrogen bonds seem to be less affected. Various experimental evidence supports this assumption. The T_g of polyamides varies with chain rigidity (for instance, nylon-6,6 has a T_g of 50 °C and 6I nylon of 126 °C), although the hydrogen bond strength is similar, as can be attested by FTIR measurements (the position of the NH valence vibration does not vary significantly for nylon 6/6,6/6,10[24] or 6IcoT nylon,[25] for example). Furthermore, temperature studies of various nylons have shown that the intensity increase of the free NH band, which was previously thought to be related to breaking of hydrogen bonds, is mainly due to variations in absorption coefficients with temperature.[24] It has been proposed that hydrogen bonds of nylons are hardly broken around T_g and only vary significantly approximately 20 °C before melting,[24] contrarily to previously held belief.

Although variations in hydrogen bonds would undoubtedly alter the T_g of polyamide or polyamide blends, T_g–composition behavior is likely to be affected in great part by weak, van der Waals type interactions as well as by longer-range electrostatic interactions.

Figure 4 illustrates the dependence of T_g on composition, before and after crystallinity correction. As can be seen, two main behaviors are observed: negative deviations from linearity for the nylon-6,5, nylon-6,7, and nylon-6,9 blends and an S-shaped curve for the nylon-6,8 blend. The corrections for crystallinity did not alter much the T_g–composition curves, except in the case of the nylon-6,5 blend, which seemed to follow slightly an S-shape before correction, whereas after correction the curve was found to adopt, within experimental error, a slightly convex shape. Three theories will be used to account for both convex and S-shaped curves: those of Kwei,[11] Lu and Weiss,[12] and Brekner, Schneider, and Cantow.[13]

Evaluation of Interactions Using the Kwei Relationship. Kwei[11] has modified the Gordon-Taylor equation to take into account positive, negative, and S-shaped deviations,

$$T_{g_{\mathrm{blend}}} = \frac{w_1 T_{g_1} + k w_2 T_{g_2}}{w_1 + k w_2} + q w_1 w_2$$

where q, an empirical parameter, is related to the strength of interchain interactions. Using the Kwei relationship, deviations are fitted using the q and k parameters. Originally, q was proposed to be proportional to the number of specific interactions in the blend (hydrogen bonds, charge transfer, etc.), since for various systems the formation of hydrogen bonds was related to a positive deviation of the T_g–composition curve. Negative deviations were less straightforward to justify. Lin, Kwei, and Reiser[26] proposed that q should be related to the stabilization energy of the backbone in excess to the weighted average of the components. A negative q value would be related to weaker backbone interactions, which would result in a higher energy. For the blend to be miscible, the overall energy of the system must be favorable. The high energy was proposed to be counterbalanced by side-chain interactions and alignment, which effect T_g only marginally.

The nylons studied here have no side chains, so this interpretation cannot be used. The polymer can however be separated into portions of the chain which undergo long-range movements at T_g as compared to portions less affected by such movements. The flexible, aliphatic segments, for which van der Waals interactions are disrupted at T_g, could be less well organized in the blend. Resulting weaker van der Waals interactions, resulting in lower T_g values, would however mean a higher energy, which is incompatible with miscibility. Miscibility could then result from entropy effects. The higher energy could also be compensated by a better alignment of hydrogen bond forming groups, which would result in a narrower distribution of hydrogen bond geometries without affecting T_g appreciably. FTIR spectroscopy studies have been undertaken to shed light on this aspect.

Following this line of reasoning, q would be related to the relative strength of van der Waals interactions between segments of the blends. It is interesting to note that a similar conclusion was reached using molecular modeling of *n*I nylon/mpI blends.[7] The q values obtained in this previous study were similar to those obtained for the present blends when assuming that $k = 1$: the present values range from −46 to −196, whereas values of −70 and −141 were obtained for 6I nylon and 7I nylon blends with mpI, respectively. Van der Waals interactions are therefore likely to be stronger for the nylon-6,5 blend with 6I nylon blend, intermediate for the nylon-6,9 blend, and weaker for the nylon-6,7 blend.

In the case of S-shaped curves, such as the one observed for the nylon-6,8/6I nylon blend, k and q are both used as fitting parameters. Lin and co-workers propose that this type of curve results from increased to decreased backbone stability pertaining to two different molecular morphologies. It is readily conceivable that, depending on the nature of the polymer forming the bulk of the amorphous phase, interactions between two different chains are liable to induce different conformations, leading to morphology changes. The occurrence of these two morphologies is however proposed to be a sign of incipient phase separation.[26] In the present study, no experimental indication for such a phase separation was observed for the blend showing an S-shaped behavior. Furthermore, preliminary FTIR results, which will be the object of a forthcoming paper, show that, on the molecular level, the amide groups seem intimately interconnected. Of the two systems where melting was necessary to induce miscibility, which could have been due to "borderline miscibility", none showed an S-shaped curve. It is interesting to note that only the even–even nylon shows this type of S-shaped curve, the even–odd nylons showing negative deviation curves. It is well known that odd–even effects can affect conformations and packing energies of chains in the crystal phase.[27] It is possible that similar effects are also present in the amorphous phase and therefore in the blends. In particular, the relative orientation of successive amide groups is related to the parity of the chain and is liable to affect the hydrogen bond network of the amorphous phase. Further work will be necessary to investigate the possible influence of the parity of the chains on miscibility, T_g–composition relationship, and conformational changes in the amorphous phase of miscible blends.

Table 3. Comparison of χ Parameters Calculated for Various Blends Using the Lu and Weiss Equation[12]

blend	χ_{min}[a]	χ_{max}[b]	χ_{crit}[c]
6,3/6I			0.082
6,4/6I			0.038
6,5/6I	−0.025	0.025	0.031
6,6/6I			0.035
6,7/6I	0.050	0.190	0.031
6,8/6I	0.020	0.120	0.031
6,9/6I	0.010	0.070	0.029
6,10/6I			0.073

[a] Minimum χ value calculated using observed T_g for all compositions and the Lu and Weiss equation. [b] Maximum χ value calculated using observed T_g for all compositions and the Lu and Weiss equation. [c] Critical χ value representing the entropy contribution of the system.

Calculation of the χ Interaction Parameter Using T_g. A different modification of the Gordon–Taylor relationship has been proposed by Lu and Weiss, which relates T_g to interactions through the use of the χ thermodynamic interaction parameter:[12]

$$T_g = \frac{w_1 T_{g_1} + k w_2 T_{g_2}}{w_1 + k w_2} - \frac{\chi R (T_{g_2} - T_{g_1}) b w_1 w_2}{\Delta C_{p_1} (w_1 + k w_2)(w_1 + b w_2)^2}$$

where b is the ratio of amorphous densities of polymer 2 and polymer 1 and ΔC_p can be approximated by

$$\Delta C_p(T_g) = 63 + 0.17 T_g$$

In this approach, each T_g–composition pair leads to a different value of χ. These have been calculated using the approximation that amorphous phases have the same density ($b = 1$), and k values have been estimated by the ratio of ΔC_p, as proposed by the authors. Minimum and maximum values obtained for the measured compositions are reported in Table 3, along with the critical χ value that represents the entropy contribution to the system,

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

where N represents the degree of polymerization.[28] χ_{crit} therefore represents the χ value that must not be exceeded by the system in order to obtain a miscible blend, or the tolerance that entropy affords to unfavorable interaction interactions.

A striking observation can be made when comparing the χ values obtained from experimental T_gs and the critical values: χ_{crit} is insufficient to account for the positive χ value observed. Nevertheless, miscibility is observed. The cause for discrepancy must lie in the evaluation of entropy or enthalpy. Entropy evaluation through χ_{crit} is based on thermodynamic equations determined for blends showing weak, nondirectional forces, which may therefore lead to large errors when applied to hydrogen bond forming blends. In terms of enthalpy, approximations of b and k could have led to an overestimation of χ, or the use of T_g itself for the estimation may be a source of error. As mentioned earlier, at T_g, hydrogen bonds are not broken. This value could therefore be leading to an estimation of the van der Waals contribution to χ only in the present system. It is unfortunately not possible to use melting point depression to determine an overall χ parameter because of severe degradation problems encountered around the melt points of nylons-6,*m*.

Effect of Local Orientation on T_g. A different interpretation can be obtained through a theory proposed more recently by Brekner, Schneider, and Cantow.[13] According to this, deviations from linearity stem from two main factors: the interpretation energy of interchain contacts and the perturbations to the environment resulting from the formation of such contacts. This is expressed by

$$\frac{T_g - T_{g_1}}{T_{g_2} - T_{g_1}} = (1 + K_1)w_{2c} - (K_1 + K_2)w_{2c}^{\,2} + K_2 w_{2c}^{\,3}$$

and

$$w_{2c} = \frac{K w_2}{w_1 + K w_2}$$

where subscript "1" is given to the polymer with the lowest glass transition temperature. This theory offers a slightly different understanding of the effect of interactions on T_g.

Three variables are used: K, K_1, and K_2. K is the Gordon–Taylor variable, related to the difference in densities or to changes in the ratio of expansion coefficients. It has been approximated as T_{g1}/T_{g2} using the Simha–Boyer rule,[29] since the polymer densities are similar.

The two remaining variables, K_1 and K_2, are related to the energetics of the system. K_1 accounts for the energy difference related to the formation of heterochain contacts as well as to energetics perturbation of polymer 1, having the lowest T_g, with respect to binary interactions. K_2, on the other hand, is related solely to differences in energy related to perturbation in the neighborhood of each polymer forming the blend.

Values of K_1 and K_2 reported in Table 4 have been obtained from graphs of $(T_g - T_{g_1})/[w_2(T_{g_2} - T_{g_1})]$ vs w_{2c}, presented in Figure 5. On this figure, error bars were calculated by incertitude propagation of the first derivative of the function. The error is particularly large at low w_{2c} values, because of the $T_g - T_{g_1}$ term used in the calculation and of division by w_{2c} which is then close to zero. In this representation, the blends which previously presented convex shapes are now expressed as linear relationships. These yield values of $K_2 = 0$, which is attributed to the fact that the perturbation to the environment is similar for each component in the blend.

Table 4. T_g–Composition Parameters Derived from Experimental Data

	Kwei relationship		Brekner–Schneider–Cantow relationship		
	K	q	K	K_1	K_2
6,5/6I	1	−46	2.8	0.3	0
6,7/6I	1	−196	2.9	−1.5	0
6,8/6I	8.7	41	1.7	1.2	3.9
6,9/6I	1	−130	2.4	−0.6	0

Values of K_1 for these curves range from 0.3 for nylon-6,5 to −1.2 for nylon-6,7. The order of these deviations follows that observed previously using the Kwei q parameter. However, in this case, a slightly positive value is observed for nylon-6,5. The uncertainty on this value is such that its sign cannot be determined with certainty. In general, negative K_1 values are therefore observed. Since the interaction energy cannot be unfavorable, or else immiscibility would result, the perturbation that interactions have on the environment with respect to pure polymer 1 must be responsible for the negative values of K_1 observed in both cases.

Brekner, Schneider, and Cantow[30] propose that the environment effect is mainly an orientation effect: the presence of heterochain contacts induces conformational rearrangements in the neighborhood of the contacts, which in turn induce chain parallelism or orientation. This results in a positive K_1 value. When heterocontacts do not lead to orientation, on the other hand, K_1 is negative, and the resulting T_g can even be lower than that of the pure polymer.[31] This "orientation" effect could be related to changes in short-range order which has been proposed to exist in the amorphous phase of polymers. Unfortunately, for the present systems, the presence of strong diffraction peaks due to the crystalline phase partly overlap the amorphous scattering. Furthermore, low-intensity diffraction peaks occurring at high diffraction angles are invariably large and would be very difficult to separate from the scattering pattern of the amorphous phase. It is therefore very difficult to use X-ray scattering, which is the most common method to investigate short-range order,[32] on these systems.

This interpretation is in apparent contradiction with the behavior proposed using the Kwei theory. Both can however be conciliated. The overall order may be decreased in spite of the increase in order of the hydrogen bond network because of aliphatic and aromatic chain rearrangements, leading also to changes in van der Waals energy.

Brekner, Schneider, and Cantow also emphasize the importance of component-specific parameters, such as conformational energy barriers, which affect indirectly the K_1 and K_2 parameters. Changes in conformations resulting in heterochain hydrogen bond formation and van der Waals interactions may indeed result in lower conformational energy barriers in relation to the movements nascent at T_g.

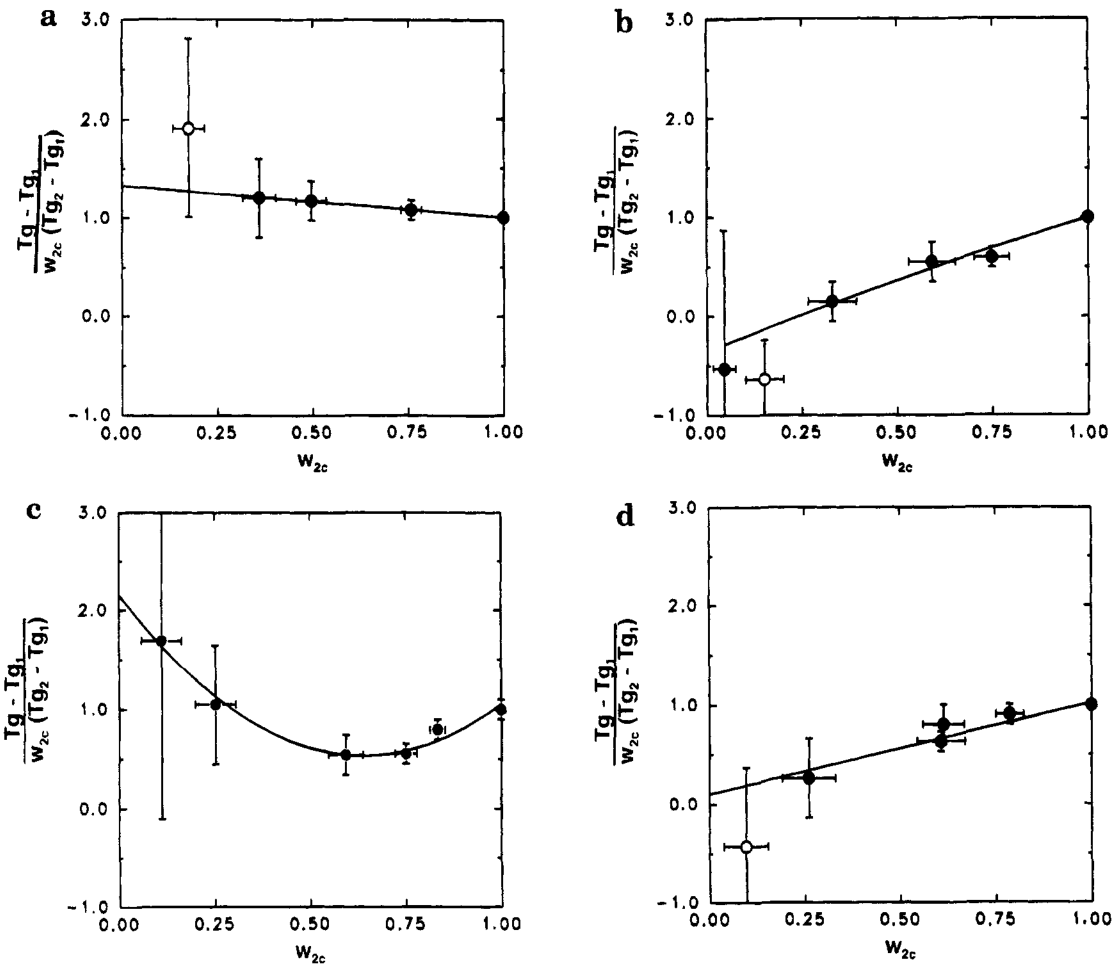

Figure 5. Application of the Schneider relationship to miscible blends: (a) nylon-6,5/6I nylon blend; (b) nylon-6,7/6I nylon blend; (c) nylon-6,8/6I nylon blend; (d) nylon-6,9/6I nylon blend.

The nylon-6,8/6I nylon blend, which previously showed an S-shape, is now represented as a curve deviating from linearity, with K_2 taking a nonnegative value. The K_1 value is positive for this blend, which indicates that either the energy difference related to heterochain contact formation or the perturbation energy of polymer 1 with respect to heterochain interactions is negative and therefore favorable to miscibility. The K_2 value indicates, as stated previously, an important effect of the interacting pair on the homopolymers. In this respect, the interpretation is similar to that of Lin and co-workers,[26] although it is not suggested that this is a sign of incipient phase separation. In view of the Brekner, Schneider, and Cantow theory, it could be proposed that the formation of hydrogen bonds, which leads to favorable interachain interacations, induces an orientation effect in one of the polymers and not in the other. This effect would therefore be different for a polymer 1-rich blend as compared to a polymer 2-rich blend, which is interpreted as the presence of two "conformations". No experimental evidence exists at this point to verify whether this effect is related to phase separation or not.

Conclusions

The general aim of this work was to afford a better understanding of the miscibility of strongly interacting polymers. Two aspects were emphasized: The effect of chain length variations on miscibility, and the relationship between the T_g–composition information and interaction changes in the blends.

It has been shown, using nylon-*n*,*m*/6I nylon blends, that composition of the repeat unit was not the sole factor affecting miscibility: the length of the aliphatic chains between amide groups played a major role. Chain parity is also suspected to be an important factor, although further experimental evidence will be necessary to verify this point. Variations of chain length for a same chemical composition of the repeat unit was interpreted as being related to average interamide distance fluctuations, which were proposed to be related to miscibility in the first article of this series. Limitations of the previously proposed rule of thumb were enlightened, as were those of the binary interaction model. No good prediction method therefore exists, at this moment for homopolyamide blends, although both the rule of thumb and the binary interaction model are useful for a first screening.

Various theories have been reviewed in order to relate T_g to miscibility and to interaction formation at the molecular level. These lead to slightly different interpretations. The Kwei[11] and the Lu and Weiss[12] theories both indicate lowering of the interactions. It is not clear from the present study whether the observed miscibility is due to entropic effects or to a low sensitivity of T_g to some of the interactions present in the blends. Lowering of the van der Waals interactions between nonamide groups, leading to negative deviations in T_g, could be counterbalanced energetically by ordering of hydrogen bond forming amide groups, which have less effect on T_g. S-shaped curves are attributed to systems where two different chain arrangements are possible depending on the polymer most abundant in the amorphous phase.

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