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# Miscibility of Polyamide Blends. 1. Molecular Modeling of Poly(*n*-methyleneisophthalamide)–Poly(*m*-phenyleneisophthalamide) Blends

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ABSTRACT: The miscibility of blends of two polyamides, poly(*n*-methyleneisophthalamide), or *n*I nylons, for $n = 3$–9 and poly(*m*-phenyleneisophthalamide), or mpI, has been investigated by using differential scanning calorimetry. For the polymers studied, only the blends with $n = 6$ and $n = 7$ were found completely miscible at all concentrations. Partial miscibility was observed for the 8I nylon/mpI and the 9I nylon/mpI blends. The results are confronted to current predictive methods, and possible causes for the discrepancy between predicted and observed behavior are discussed. A correlation between miscibility and the number of atoms forming hydrogen bonds per the number of non-hydrogen atoms in the repeat unit of the polymers has been noted. It is believed to stem from the energy contribution of the hydrogen bonds in the miscible blends and is proposed as a rule of thumb for the miscibility prediction for systems forming strong hydrogen bonds, in particular when the $\chi$ parameters are not known. Molecular modeling has been used for the first time to investigate the formation of interchain hydrogen bonds in the blends and is proposed as an aid for the study of miscibility in systems where strong hydrogen bonds occur.

## Introduction

The prediction of the miscibility of polymers has been a continuous subject of interest for researchers from both industrial and academic fields. Many methods have been proposed alternatively to predict this behavior. Among these, the solubility parameter approach of Hildebrand[1] has been found to be very useful. However, its validity appears to be mostly limited to cases where no specific interactions, such as hydrogen bonds, are present. This precludes the use of this method for polyamide blends.

Two very widely used approaches are the Flory–Huggins lattice theory and the equation of state thermodynamics treatment. Both methods require the knowledge of the $\chi$ interaction parameters. However, for polyamides, these parameters are not known because of the limited number of miscible polyamide blends in the literature. Very few miscible blends involving polyamides were known until recently. Zimmerman and co-workers[2] have reported a few miscible or partly miscible blends. Verma and co-workers[3] have investigated blends of commercial nylons but only report immiscible blends. Nylon-6 and nylon-6,6 blends have been investigated by Ong and co-workers[4] and were also found to be immiscible. More recently, miscibility has been reported for blends of nylon-6 and polyacrylic acid.[5]

The work of Ellis is currently increasing the knowledge of the miscibility of polyamide blends. In his early work, Ellis[6] noted the correlation between miscibility and the ratio of amide functions in the repeat units. Although he mentioned the possibility that intermolecular amide–amide interactions could explain this observation, he rejected this explanation in favor of the binary interaction model, first developed for copolymers[7,8] but which has been proposed to be valid for homopolymers.[9] This theory is based on the concept that the miscibility of copolymers is induced by repulsion or attraction of the sequences. However, in the treatment of Ellis,[10,11] no provision is made to take into account the disruption of the hydrogen bond network in the blend. The hydrogen bonds are an important feature of polyamides and are responsible for their outstanding properties (high melting point, good mechanical properties, insolubility in common solvents, etc.).

This approach is radically different from that of Painter and Coleman, who have studied the thermodynamics of blends of pairs comprising a highly hydrogen-bonding polymer (either a polyamide or a polyurethane) with a second polymer that can only receive such bonds and is only weakly self-associating.[12–14] Their work highlights are importance of the formation and disruption of hydrogen bonds in these systems. They propose that the assumption of a mean field to account for contacts between polymers (which is used both in the Flory–Huggins theory, on which the binary interaction model is based, and in the equation of state theory) is not valid when directional contacts are present. Instead, they propose an association model in which hydrogen bond formation and disruption are described by equilibrium constants that are amenable to infrared measurements.[15,16]

It may also be significant that no miscible blend involving a polymer forming strong hydrogen bonds, such as polyurethane, polyamide, or cellulose, has been reported with a polymer incapable of forming or accepting hydrogen bonds.

In light of these observations, it seems highly surprising that a method that does not take directly into account the interactions between the amide groups of the polymers in the blend would lead to accurate predictions. The most probable types of interactions between the amide groups are interpolymer hydrogen bonds, such as those reported by Coleman and Painter.[12–14]

The association model is very effective in describing the thermodynamics of the system but still relies on experimental characterization of a blend in order to determine the equilibrium constants. The method of Ellis is interesting in that it allows prediction of the miscibility on the basis of the knowledge of the nature of the repeat units alone. However, although it is proposed to explain the miscibility of homopolymers, the three systems that he has investigated until now all include one copolymer: nylon 6I-*co*-6T, Trogamid T (which is composed of a series of isomeric methylated chains), and a cycloaliphatic copolyamide. In copolymers, the intergroup repulsion may

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Table I
Viscosity and Molecular Weights of the Polymers in This Work

|  | $\eta_{\text{inh}}$,[a] mL/g | [$\eta$], mL/g | $M_v$, $10^4$ g |
|---|---|---|---|
| 3I nylon | 88 | 95 | 2.8 |
| 4I nylon | 74 | 79 | 2.2 |
| 5I nylon | 65 | 69 | 1.9 |
| 6I nylon | 80 | 86 | 2.5 |
| 7I nylon | 66 | 70 | 1.9 |
| 8I nylon | 61 | 64 | 1.7 |
| 9I nylon | 64 | 68 | 1.8 |
| 10I nylon | 60 | 53 | 1.7 |
| mpI | 55 | 42 | 0.88 |

[a] For a concentration of 0.5 g/mL.

well be preponderant for the miscibility behavior, since the hydrogen bond network is already affected by the irregularity of the copolymer structure, and its disruption during blending may limited. This may not be the case for blends comprising two homopolymers. For this reason, a system composed solely of homopolymers, in which it is believed that the hydrogen bond formation plays an important role, will be used to reinvestigate the binary interaction model.

The series of regular aliphatic–aromatic polyamides that will be studied, the poly(*n*-methyleneisophthalamides), abbreviated *n*I nylons, are known to be semicrystalline[17] but, under normal conditions, have a very low degree of crystallinity. These will be blended to poly(*m*-phenyleneisophthalamide), abbreviated mpI, which is a semicrystalline polymer known commercially under the name of Nomex (Du Pont) and for which the crystalline structure is known.[18,19] These polymers have been chosen for the similarity of their repeat units, where the aliphatic chain of *n*I nylons is replaced by a meta-substituted aromatic cycle in mpI. The aim is to determine the optimum aliphatic chain length that can replace such a meta-substituted aromatic cycle and to ascertain the effect of this substitution on the blend formation and on the formation of interpolymer hydrogen bonds. Possible correlations of the volume ratio and length of the aliphatic chain with respect to the aromatic sequence of the mpI will be investigated. The importance of the hydrogen bond formation on the miscibility and the validity of the binary interaction model for this system will be discussed. Molecular modeling, which is used extensively for drug design, polymer crystal structure resolution, etc., will be used for the first time as an aid to the understanding of the miscibility at the molecular chain level. The possibility of using molecular modeling as a method of miscibility investigation for polymers forming strong, directional interactions such as hydrogen bonds will be discussed.

## Experimental Section

**Synthesis and Characterization of the Homopolymers.** The synthesis of *n*I nylons, for *n* = 3–9, has been conducted by interfacial polycondensation following the method of Beaman and co-workers.[20] Viscosity measurements of *n*I nylons were performed in $H_2SO_4$ by using a Ubbelohde viscosimeter at 25 °C and are reported in Table I. The Mark–Houwink parameters for 6I nylon were taken from ref 21 ($K = 3.24 \times 10^{-2}$ g mL$^{-1}$, $a = 0.78$) and were used to calculate the average molecular weight of this polymer. The values of the Mark–Houwink parameters are not known for the other *n*I nylons, but it was surmised that the values for 6I nylons should give a good approximation for the other *n*I nylons and were therefore used to evaluate the molecular weights. It must however be emphasized that this approximation is best when *n* is close to 6.

The synthesis of mpI was performed by solution polycondensation as described by Morgan.[22] Viscosity was measured in *N*-methylacetamide containing 5% LiCl, and the molecular weight was calculated by using the Mark–Houwink coefficients of ref 23 ($K = 38.6 \times 10^{-3}$ g mL$^{-1}$, $a = 0.77$).

**Preparation and Characterization of the Blends.** Since the mpI polymer degrades without melting around 450 °C, even under vacuum, the blends were prepared by coprecipitation of the polymers from a $H_2SO_4$ solution. The precipitates were filtered and dried for 2 weeks under vacuum at 80 °C.

DSC measurements were performed on a Perkin-Elmer DSC-2 at a rate of 40 °/min. For blends, care was taken not to reach the decomposition temperature of the *n*I polymers, which was around 260 °C. Since the $T_g$ of mpI is higher than this value (the onset of the glass transition is observed at 268 °C), it was not possible to ascertain the absence of a $T_g$ near that of the mpI in the blends. Therefore, only two criteria were used to determine the miscibility: the absence of a $T_g$ near that of the corresponding *n*I nylon and the presence of a $T_g$ of a value intermediate between those of the two pure polymers. The $T_g$ values for the middle of the transition are reported in Table II. In all cases, only one transition could be recorded.

**Molecular Modeling of the Blends.** Molecular modeling was performed by using ALCHEMY II, a program commercialized by TRIPOS Associates, Inc. Although not as powerful as other existing molecular modeling systems, it offers the advantage of being available at a low cost, of working on widely available IBM compatible microcomputers, and therefore of being potentially accessible to most of the scientific community. For these reasons, it has been used in this first study of molecular modeling of blends, although other similar programs can be substituted. ALCHEMY II allows the calculation and the minimization of the energy of molecules. The bond stretching, angle bending, torsion deformation, out of plane bending, and van der Waals interaction energy contributions are calculated.

Hydrogen bonds are usually quantified via a Lennard-Jones 6–12 potential energy function, which reflects the electrostatic nature of this bond. In this case, in order to simulate their formation and to impose a correct geometry for these bonds, the hydrogen bonds were defined as covalent bonds. Fictive oxygen and hydrogen atoms, labeled $O_B$ and $H_B$ respectively, were defined in the amide group. These could accept an additional bond. A $O_B \cdots H_B$ bond distance of 2.08 Å and $N\text{–}H \cdots O_B$ and $H_B \cdots O_B\text{–}C$ bond angles of 162° and 160° were defined, in accordance with a study of model compounds of polyamides.[24] The default value of 300 kcal mol$^{-1}$ Å$^{-2}$ was given for the $O_B$–$H_B$ bond (approximately half of the value for an aliphatic carbon–carbon bond, which is 740 kcal mol$^{-1}$ Å$^{-2}$), and the angle bonding force constant was given the same values as those of the sp$^3$ carbon atoms (0.024 kcal mol deg$^{-1}$). The value of the van der Waals interaction constant for the interaction between these new oxygen and hydrogen atoms was set to a value of zero. The force field was left unaltered apart from these changes.

It must be noted that, while these definitions provide an effective way to fix a reasonable hydrogen bond geometry, the energy derived is not accurate, since the constants used in the description of the energy of the hydrogen bond are fixed arbitrarily. The values of the energy will therefore be used only for comparative purposes with compounds containing the same number of hydrogen bonds. It must also be stressed that the energy calculation does not include the stabilizing energy of the hydrogen bonds, which are defined, energy-wise, as regular covalent bonds.

Minimization was performed iteratively on all models until the total gradient (the sum of the first partial derivatives of the energy terms) dropped below the square of the threshold or the difference of energy between two iterations dropped below the threshold, which was fixed at 0.1.

Two hydrogen-bonded chains of each homopolymer were built and their energies minimized for comparison purposes with the blend pairs. In the case of the homopolymers, as in the case of the blend pairs, the minimization was performed on models consisting of two chains, which consisted of three amide groups and three non-amide groups (aromatic cycle or aliphatic chain). In this way, two hydrogen bonds could be defined between the two chains for all polymer pairs.

The minimization of the crystal structure conformation of mpI was performed. For the *n*I nylons, an entirely trans conformation of the aliphatic chain was used; 30° dihedral angles were set

Table II
Experimental Values of $T_g$ for *n*I Nylon–mpI Blends

| composn of *n*I nylon, % | $T_g$, °C | | | | | | |
|---|---|---|---|---|---|---|---|
| | $n = 3$ | $n = 4$ | $n = 5$ | $n = 6$ | $n = 7$ | $n = 8$ | $n = 9$ |
| 100 | 169 | 152 | 138 | 125 | 104 | 106 | 103 |
| 90 | 168 | 153 | 139 | 141 | 108 | 105 | 102 |
| 75 | 167 | 154 | 138 | 156 | 120 | 106 | 103 |
| 50 | 169 | 153 | 138 | 185 | 157 | 122 | 108 |
| 25 | 169 | 153 | 139 | 208 | 200 | 122 | 126 |
| 10 | 167 | 152 | 139 | 243 | 236 | 118 | 150 |
| 0 | 273 | 273 | 273 | 273 | 273 | 273 | 273 |

between the aromatic and the amide planes. In the case of 6I and 8I nylons, the $\tau$ torsion angles were fixed in a trans conformation, whereas for the 5I and 7I nylons, the $\tau$ torsion angles were set to 90° and −90°, as was the case for one of the model compounds of 7T nylon, 7DBN.[24] This conformation permitted the formation of hydrogen bonds between the two chains more easily than when the $\tau$ torsion angles were trans. For the homopolymers, since no symmetry element was imposed, the conformations of both chains of the pairs are slightly different from one another after minimization.

Two-chain hydrogen-bonded models of the blended polymers were built. The two polymer chains were first attached by one hydrogen bond, and variation of the conformations was performed interactively on both polymer chains until the distance between the parallel amide groups was such that a second hydrogen bond could be formed between the two chains, while conformational angles did not deviate significantly from the expected values of the previous analysis. This model was then refined by iterative energy minimization.

## Results and Discussion

**Miscibility of the Polymers.** In order to study the miscibility of true homopolymers, it is necessary to take into account the possibility of transamidation reactions, which are well-known in melted polycondensation polymers and which have been used to enhance compatibility and miscibility.[2] Transamidation has been studied and is known to result eventually in random copolymers.[25] However, the speed of the reaction varies with a large number of factors: compatibility, molecular weight, presence of water, nature of the polymers, .... It is not known to what extent this could affect the systems studied here. Consequently, care was taken during DSC measurements never to exceed a temperature of 20 °C lower that the lowest melting point of the polymers in the blend, in order to minimize the occurrence of transamidation.

Blends of *n*I nylons and mpI were studied for $n = 3$–9. Only the 6I and 7I nylons were found to exhibit miscibility for all compositions. The thermograms of these miscible blends are reproduced in Figure 1. Although broadening of the glass transition can be observed, it was insufficient to be attributed to phase separation. The lowering of the $T_g$ for some of the compositions of the 8I nylon/mpI and 9I nylon/mpI blends, as reported in Table II, is indicative of partial miscibility.

**Dependence of the $T_g$ on the Composition.** The dependence of the $T_g$ on the composition of the miscible 6I nylon/mpI and 7I nylon/mpI blends is illustrated in Figures 2 and 3, respectively. As frequently observed, the $T_g$ vs composition curve does not follow the Gordon–Taylor relationship, given by

$$T_g = \frac{w_1 T_{g_1} + w_2 T_{g_2}}{w_1 + k w_2}$$

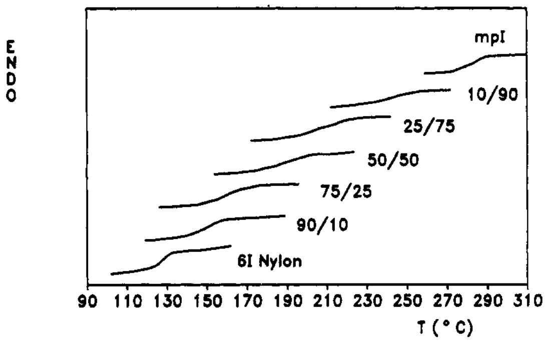
and represented, for $k = 1$, by a straight dotted line in Figures 2 and 3.

The variations of $T_g$ with composition for the miscible *n*I nylon/mpI blends can be expressed through the relation proposed by Kwei:[26]

$$T_g = \frac{w_1 T_{g_1} + w_2 T_{g_2}}{w_1 + k w_2} + q w_1 w_2$$

In must be noted that the equation of Schneider[27,28] could also be used to characterize the system, and the value of $q$ can be related directly to the value of the $K_1$ parameter of Schneider. The application of the Kwei relationship, represented by a curve in Figures 2 and 3, yields values

a) 6I Nylon / mpI



b) 7I Nylon / mpI

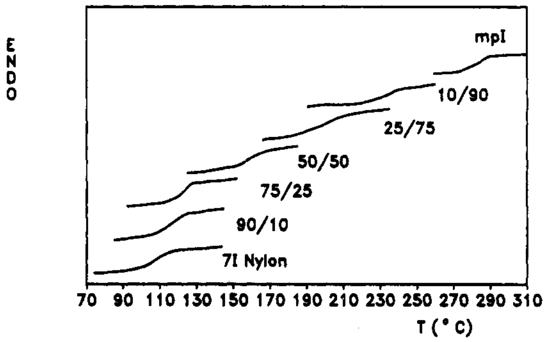


**Figure 1.** Thermograms showing the glass transition of the miscible *n*I nylon/mpI blends: (a) 6I nylon/mpI blend; (b) 7I nylon/mpI blend.

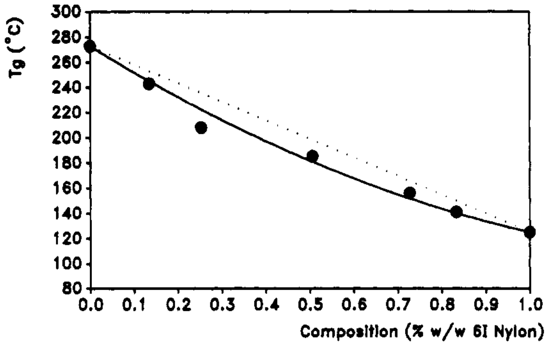


**Figure 2.** Dependence of the glass transition temperature on composition for the miscible 6I nylon/mpI blend.

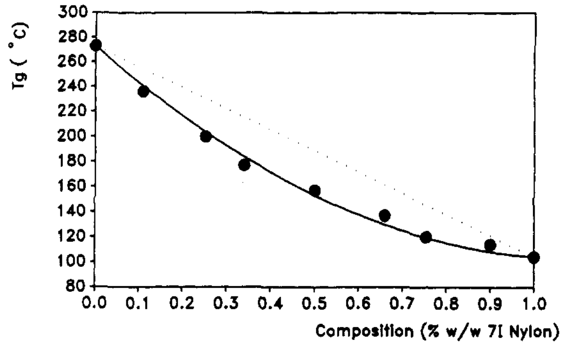


**Figure 3.** Dependence of the glass transition temperature on composition for the miscible 7I nylon/mpI blends.

of $q = -70$ for the 6I nylon/mpI blends and $q = -141$ for the 7I nylon/mpI blends.

Deviations from the Gordon–Taylor equation, quantified by the factors $q$, have been proposed to stem from variations in the efficiency of the hydrogen bond formation.[26] However, recent work of Kwei and coworkers[29,30] has shown that the hydrogen bond formation is not the sole factor affecting the value of the $T_g$ in a blend. The $T_g$ phenomenon, which is related to segmental motions in the polymer, is affected by steric hindrance and variations of the flexibility of the chains. It is therefore postulated that $q$ can be related both to hydrogen bond formation and to changes in the environment of the chains.

The lower value of $q$ for the 7I nylon/mpI blend would consequently indicate a lower propensity to hydrogen-bonding formation, a lower flexibility of the polymer chains than that of the 6I nylon/mpI blends, or a combination of both effects.

**Prediction Using the Binary Interaction Model.** One of the aims of this work was to test the binary interaction model on a system composed of a series of two true homopolymers forming strong hydrogen bonds. These are composed of $A_yB_zC_{1-y-z}$ and $A_rB_sC_{1-r-s}$, where A is the aliphatic portion of the repeat unit, B the amide portion, and C the aromatic portion. The value of $\chi$ for the blend is given by[7,11]

$$\chi_{\text{blend}} = [y(s-z) + r(z-s)]\chi_{AB} + [(1-y-z)(s-z) + (1-r-s)(z-s)]\chi_{BC} + [(1-y-z)(r-y) + (1-r-s)(y-r)]\chi_{AC}$$

The values of $\chi_{AB}$, $\chi_{AC}$, and $\chi_{BC}$ have been calculated from similar polyamide systems[7,11] and are

$$\chi_{AB} = 2.685$$

$$\chi_{AC} = -0.127$$

$$\chi_{BC} = 2.308$$

The values of a $\chi$ blend calculated by using this method are represented in Figure 4. The maximum probability for miscibility to occur would be for $n = 4$ according to this theory. As mentioned previously, experimental data show a maximum miscibility for $n = 6$–7. Previously studied systems[6,10,11] were predicted with surprising accuracy with this model, and by comparison the present systems show a great discrepancy between observed and predicted behavior.

What caused this discrepancy? It may be related to uncertainties in the values of the $\chi$ parameters. Another possible cause would be the use of the same $\chi$ parameters for para- and meta-substituted aromatic cycles, but previously studied systems were accurately predicted notwithstanding this effect. It may also be related to the use of a $\chi$ parameter determined for aromatic cycles attached to the carbonyl of the amide groups, whereas in our systems half of the cycles are attached to the carbonyl and half to the nitrogen of the amide functions. However, this seems a rather limited change and should not affect the $\chi$ parameter value any more than the type of substitution of the cycle.

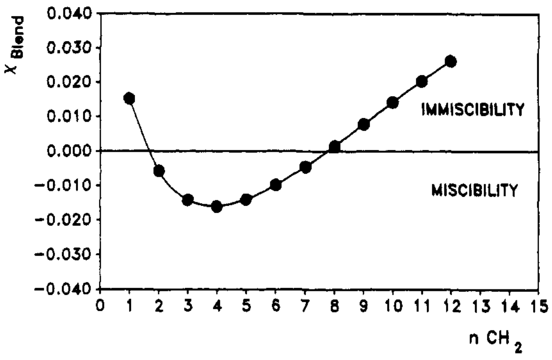


**Figure 4.** Predicted values of the $\chi_{\text{blend}}$ according to the binary interaction model.

A more fundamental cause may be underlying in this case: in the predictive model, the interactions of the groups are assumed being independent of the length of the adjacent groups. This implies that hydrogen bond formation is independent of the distance between the amide groups in each polymer. Although this might be justified for copolymers, where the distance between the amide groups vary randomly, this assumption might be too drastic for regular homopolymers. Failure to take into account the possibility of formation of hydrogen bonds between the two polymers of a blend might explain the incorrect predictions of the model. It must be stressed at this point that hydrogen bond formation between the two polymers is proposed, from the work of Painter and Coleman, to be an essential factor in miscibility. On a molecular scale, it can be conceptualized that, since all amide groups are involved in hydrogen bonding, if such bonds are not able to form between chains of the two homopolymers, the homopolymers will segregate in two phases and immiscibility with result. It is proposed, in light of the present results, that the use of the binary interaction model should be restricted to systems containing at least one copolymer until further work permits refinement of the model, either to correct the inaccuracy of the $\chi$ parameters or to add a term to take into account the effect of the interchain hydrogen bond formation on the blend.

**Predictions Based on the Amide Group Proportion.** As observed by Ellis,[6] the miscibility seems to be related to the proportion of amide groups in the polymers. The volume fractions have been commonly used in thermodynamical calculations of blends and might provide a useful comparison basis. The volume fraction of the amide groups of the repeat units of the polymers has therefore been calculated from the values of the group contributions to the molar volumes taken from ref 31 and appears in Figure 5. Similar volume fractions of the amide groups are noted for the 4I nylon and mpI. This result cannot directly be related to the miscibility.

A striking feature of the systems studied here is that a meta-substituted aromatic cycle has been replaced by an aliphatic chain composed of a similar number of carbon atoms (from 6–7 experimentally). It would seem more appropriate, on the basis of this experimental result, to compare the proportion of non-hydrogen atoms receiving

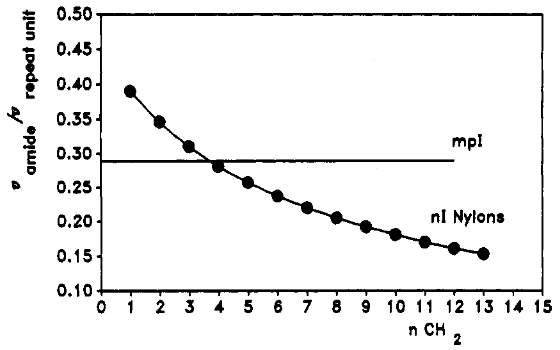


**Figure 5.** Volume fractions of the amide groups in the repeat units of the polymers.

or giving hydrogen bonds as compared to the total number of non-hydrogen atoms in the repeat unit for each polymer in the blend. Indeed, although this does not permit a perfect prediction of the miscibility of the systems involved in this study, this simple observation can be used as a rule of thumb to determine the miscibility possibilities. It could be particularly useful in cases where the values of the $\chi$ parameters have not been determined.

As mentioned previously, few polyamides have been found to form miscible blends. Among these, nylon-6 and polyacrylic acid[5] roughly obey this rule; for nylon-6 and polyacrylic acid, this proportion is similar: 1:4 as compared to 1:3. The miscible blends reported by Ellis[6,10,11] all include one copolymer. Nevertheless, the proportion of hydrogen-bonding atoms also follows the miscibility changes: Trogamid T has a proportion of 1:5.25 and is found miscible with polymers having proportions of 1:4 to 1:5.5 (nylon-6, nylon-6,6, nylon-6,9, nylon-6,10, nylon-6,12, and nylon 6I-*co*-T) while it is nonmiscible when this proportion falls lower than 1:4 (nylon-4, nylon-4,6) or is higher than 1:5.5 (nylon-11, nylon-12). Similarly, nylon 6I-*co*-T, which as a proportion of 1:4.5, is found to be miscible to polyamides, for which proportions vary from 1:3.5 to 1:4.75, and is immiscible with polymers having a proportion falling outside this range, with one exception: that of a cycloaliphatic copolyamide for which the proportion was 1:5.04. This exception illustrates the limitations of this rule of thumb. The proportion of hydrogen-bonding atoms in the repeat unit appears to give, for the known miscible polyamide blends, a good approximation of the possibilities of formation of miscible blends, although it does not permit the prediction of the limits of the miscibility window, and is admittingly not the sole factor affecting miscibility. The small number of miscible blends comprising strong hydrogen bonds does not allow us to ascertain the limits of validity of this rule.

This observation can in no way be related to existing thermodynamical treatments. However, it might be postulated to be related to hydrogen bond energy of the polymers and might therefore eventually be related to the enthalpy of formation of miscible blends, although further work will be necessary to verify this hypothesis.

**Modeling of Interpolymer Hydrogen Bond Formation.** The second part of this work is directed toward the comprehension, and possibly prediction, of the hydrogen bond formation, at the molecular level, between two homopolymers. It is hoped that eventually such an approach could be used to circumvent the limitations of the binary interaction model.

It must be stressed that the formation of hydrogen bonds is not the sole factor governing the miscibility of the blends, but the thermodynamical treatment of Painter and Coleman deals with the quantitative aspect of the miscibility and will not be investigated further. Instead, in the following section, it will be attempted to relate the changes in local energies associated with hydrogen bonding, as investigated by molecular modeling, to the miscibility behavior of the blends.

In order to build a model as simple and, at the same time, as representative as possible, the work has been separated in three successive sections. In a first section, a review of the present knowledge of possible conformations and degrees of freedom of the polymer will first be made.

In a second step, models representing the maximum extension of the chains will be built, and the amide–amide distances will be calculated from these models. Comparison of these distances for each polymer blend will be discussed in relation to the observed miscibility.

The third, and more important step, will consist of a molecular modeling of the interactions in the blend. In this section, the understanding of the influence of hydrogen bond formation at the molecular level will be discussed.

**(a) Conformation of the Homopolymers.** Each of the polymer chains of the blend comprises an important number of possible conformations. In order to simplify the modeling, the conformational information gained from the study of the crystal structures of the polymers and of related compounds will be reviewed. A definition of the various torsion angles used to define the conformations of the polymer chains is given in Figure 6.

In the case of mpI, the crystalline structure is known and conformational analysis has been performed previously.[18,19] The flexibility of the mpI chain is limited: the only rotational degrees of freedom are around the bonds between the aromatic cycles and the amide groups. These rotations are hindered by the resonance between the amide groups and the aromatic cycles. In spite of this resonance phenomena, the torsion angles $\tau$ and $\epsilon$ between the amide group and the aromatic cycle deviate from planarity because of the interactions between the ortho hydrogen atoms of the cycle and the O and H atoms of the amide group. Potential energy calculations predict a minimum at ±31 or ±149° for the $\tau$ torsion angle and at ±25 or ±155° for the $\epsilon$ torsion angle.[18]

The most striking feature in the crystal structure of mpI is the formation of hydrogen bonds in two directions roughly perpendicular to one another and to the direction of the chain elongation. This is allowed by an appropriate combination of $\tau$ and $\epsilon$ torsion angles ($\tau_{m1} = -38°$, $\tau_{m2} = 153°$, $\epsilon_{m1} = -146°$, and $\epsilon_{m2} = -32°$). It has been proposed that this conformation is necessary for hydrogen bond formation to occur, because of high steric interactions when the amide groups are in the same plane.

For the *n*I nylons, for which the crystal structures have never been investigated, previous studies of *n*T nylons, which differ from *n*I nylons only by the substitution of the aromatic cycle (para as compared to meta), will be used to determine the possible conformations. From the studies of the *n*T nylons and of their model compounds,[24,32–34] it can be surmised that the $\epsilon$ torsion angles is subject to the same effects as in the mpI polyamide. The average value for this torsion angle is near ±30° or ±150°, with variations of approximately 10°. The $\tau$ torsion angles show a much greater flexibility, with values ranging from ±65° to 180°. The most common values are ±90° and 180°. The $\phi$ torsion angles of the aliphatic chain have values near 180° or ±60°.

**(b) Comparison of the Interamide Distances.** Two mpI chains have been built: one with successive +30° and −30° torsion angles, where all the amide groups are lying in the same plane, and a second one, similar to that of the

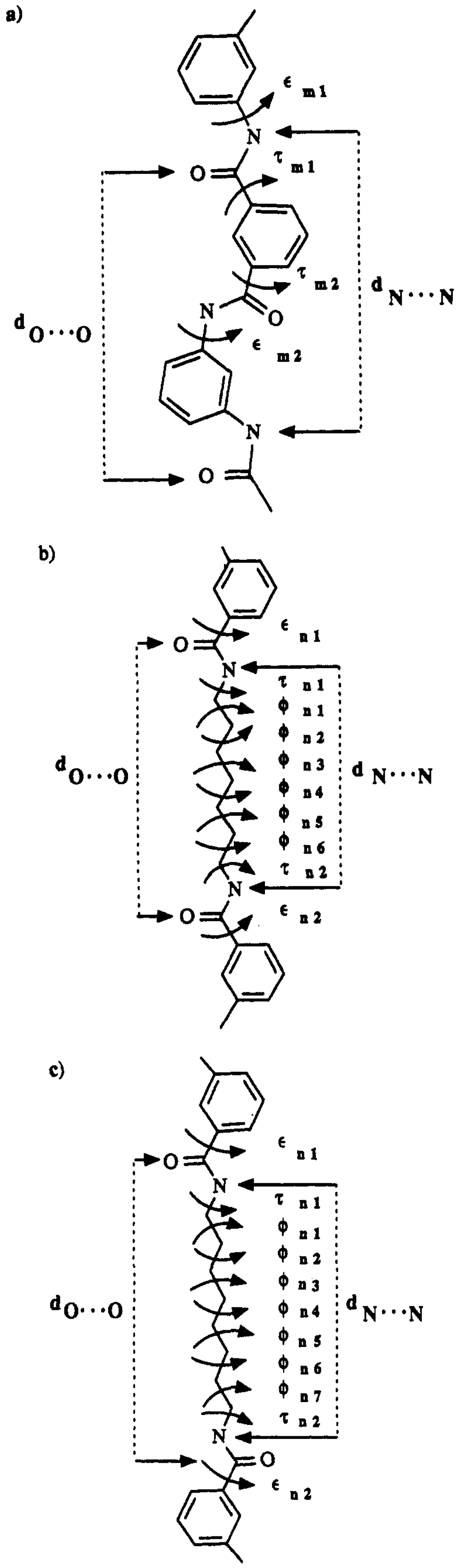


**Figure 6.** Definition of the torsion angles and of the distances between successive parallel amide groups of the polymer chains: (a) mpI; (b) 7I nylon; (c) 8I nylon.

crystal structure, with successive +30° and −30° torsion angles, which results in a 60° angle between successive amide groups.

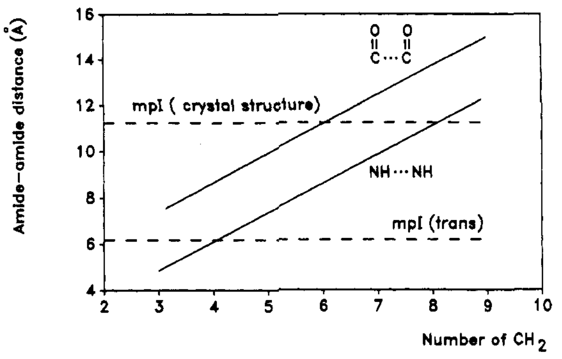


**Figure 7.** Comparison of the distances between coplanar amide groups in the homopolymer chains.

Chains of the 5I, 6I, and 7I nylons have been built by using an all-trans conformation of the chain and 30° rotations of the amide groups with respect to the aromatic moiety. These molecular models represent the maximum elongation that can be energetically favored for the chain, although they do not necessarily represent the most stable or the most probable conformations.

The distances between the two successive coplanar amide groups of *n*I nylons and mpI have been calculated by using the chains built in this way and appear in Figure 7. For the *n*I nylons, two values have been considered: the distances between successive nitrogen atoms and those between successive oxygen atoms, which are not the same, as can be appreciated from Figure 6. The *n*I nylon models built have coplanar amide groups, and therefore distances between coplanar amide groups in mpI have been considered. In the case of the first conformation, where all amide groups are coplanar, the distances are found to be comparable to those of *n*I nylons for $n = 2$–4. This is in agreement neither with the ratio of hydrogen-bonding atoms nor with the experimental results.

When the distance of the crystal-structure-like conformation of mpI is compared to that of the *n*I nylons, a good match is found for $n = 6$–8, in agreement with the observed behavior of the blends. In this case, the distance between coplanar amide groups is greater since an amide group at 60° from the others is intercalated. A conformation similar to that of the crystal structure, where two successive amide groups are positioned at 60° from one another, whereas the third amide group is parallel to the first, will therefore be selected to model the interchain hydrogen bond formation in the next section.

A combination of the amide–amide distance values and of the ratio of hydrogen-bonding atoms in the repeat units can be used to predict with reasonable accuracy the miscibility of this system, although it is not known at this stage whether this technique could be used systematically. Its use on copolymers, where amide–amide distances can vary considerably along the chain, is doubtful, but for homopolymers it might provide interesting indications.

**(c) Molecular Modeling of the Interchain Hydrogen Bond Formation in the Homopolymers and in the Blends.** Our understanding of the amorphous phase is still fragmentary. It has been established without doubt that no three-dimensional long-range order, of the type prevailing in crystals, can exist in the amorphous phase. On the other hand, models where the conformation varies randomly have been found equally unsuccessful on the basis of experimental results.[35,36] For example, the free volume of the amorphous phase is found to be considerably smaller than that predicted from the spaghetti model.[35] It is generally accepted that short-range order must be present in the amorphous phase. In the case of the polymer

**Table III**
**Torsion Angles (deg) Defining the Conformation of the Hydrogen-Bonded Chain Pairs**

| | | | | | | | nylon 6I/mpI | | nylon 7I/mpI | | nylon 8I/mpI | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | mpI | 5I nylon | 6I nylon | 7I nylon | 8I nylon | nylon 5I/mpI | a | b | a | b | a | b |
| $\tau_{m1}$ | 145.8<br>150.8 | | | | | 169.4 | 137.7 | 168.5 | 150.2 | −154.0 | 148.8 | 148.3 |
| $\tau_{m2}$ | −16.8<br>−21.6 | | | | | −42.4 | −1.6 | 15.8 | 1.8 | −10.5 | −17.9 | −4.5 |
| $\epsilon_{m1}$ | −141.4<br>−143.1 | | | | | 24.9 | 40.1 | 28.6 | 29.2 | 31.8 | 23.5 | 30.6 |
| $\epsilon_{m2}$ | −141.4<br>−143.1 | | | | | 155.2 | 152.4 | 135.5 | 149.9 | 139.8 | 154.8 | 138.1 |
| $\epsilon_{n1}$ | | −156.5<br>−158.9 | 24.5<br>27.6 | −143.2<br>−148.1 | −23.1<br>−20.9 | −157.3 | −171.7 | 163.8 | 167.1 | −29.4 | −173.0 | 149.5 |
| $\tau_{n1}$ | | 124.8<br>123.7 | −176.0<br>−170.4 | 111.0<br>111.9 | 174.0<br>172.2 | 172.6 | 94.8 | −53.4 | 141.8 | −73.7 | −92.9 | −98.4 |
| $\phi_{n1}$ | | −178.0<br>−176.9 | 180.0<br>180.0 | −177.9<br>−175.9 | 178.5<br>178.3 | −175.2 | 74.7 | −165.7 | −177.3 | 166.4 | −165.6 | 174.9 |
| $\phi_{n2}$ | | 180.0<br>180.0 | 180.0<br>180.0 | −178.5<br>−178.4 | −179.1<br>180.0 | −170.8 | −173.5 | −177.6 | 167.8 | 174.2 | −161.8 | 165.1 |
| $\phi_{n3}$ | | 180.0<br>180.0 | 180.0<br>−178.9 | 180.0<br>180.0 | 179.0<br>180.0 | 180.0 | −172.2 | −172.7 | −176.4 | 173.2 | 156.2 | −171.4 |
| $\phi_{n4}$ | | 177.6<br>176.5 | 180.0<br>178.2 | 180.0<br>180.0 | 180.0<br>180.0 | −176.2 | −160.3 | 174.0 | −178.8 | 162.4 | −176.2 | 167.5 |
| $\phi_{n5}$ | | | −179.1<br>180.0 | 180.0<br>179.0 | 180.0<br>180.0 | | −169.3 | −174.6 | 177.4 | −176.4 | 178.7 | −154.1 |
| $\phi_{n6}$ | | | | 178.0 | −180.0 | | | | −178.4 | 170.1 | 176.7 | −171.8 |
| $\phi_{n7}$ | | | | 176.4 | −180.0<br>−178.6<br>180.0 | | | | | | −172.6 | −174.4 |
| $\tau_{n2}$ | | −119.1<br>−115.7 | −176.1<br>−174.5 | −117.0<br>−113.5 | −161.3<br>−168.3 | −177.0 | 124.5 | −139.4 | −155.3 | 178.8 | −132.1 | −130.2 |
| $\epsilon_{n2}$ | | 158.6<br>156.7 | 149.1<br>147.4 | 158.8<br>156.4 | 149.1<br>148.1 | 174.0 | 161.0 | −153.2 | 162.2 | 155.6 | 162.2 | −154.2 |

**Table IV**
**Energy of the Hydrogen-Bonded Polymer Chain Pairs**

| | $E_{total}$ | $E_{bond}$ | $E_{angle}$ | $E_{tor}$ | $E_{oop}$ | $E_{vdw}$ |
|---|---|---|---|---|---|---|
| mpI | −14.4 | 0.7 | 3.8 | 17.9 | 0.2 | −37.0 |
| 5I nylon | −27.4 | 0.4 | 4.3 | 9.4 | 0.1 | −41.5 |
| 6I nylon | −24.3 | 0.3 | 3.7 | 11.0 | 0.1 | −39.4 |
| 7I nylon | −27.8 | 0.3 | 4.0 | 11.6 | 0.0 | −43.8 |
| 8I nylon | −34.8 | 0.3 | 3.5 | 10.5 | 0.1 | −49.2 |
| mpI/5I nylon | 20.1 | 1.8 | 11.0 | 24.5 | 0.7 | −17.9 |
| mpI/6I nylon (a) | −11.4 | 0.7 | 6.2 | 14.9 | 0.2 | −33.5 |
| mpI/6I nylon (b) | −10.7 | 0.5 | 4.5 | 11.9 | 0.2 | −27.8 |
| mpI/7I nylon (a) | −13.2 | 0.7 | 4.4 | 11.1 | 0.1 | −29.6 |
| mpI/7I nylon (b) | −15 | 0.6 | 3.2 | 16.3 | 0.2 | −35.3 |
| mpI/8I nylon (a) | −9.9 | 0.9 | 4.8 | 13.9 | 0.3 | −29.7 |
| mpI/8I nylon (b) | −10.3 | 0.4 | 4.4 | 16.9 | 0.2 | −32.2 |

blends, miscibility implies intimate contact between the chains in the amorphous phase. Short-range order, which must also be present in the blends, could therefore be favored by the presence of interchain interactions, which are generally held responsible for miscibility. Similarly, repulsion between segments of an homopolymer, which would be detrimental to short-range order, would favor miscibility with a second polymer since it would favor short-range order through van der Waals interactions.

For polyamides, an additional constraint is present in the form of the hydrogen bond formation, which has been known in other systems to bind chains of the two polymers forming the blend. Molecular modeling of hydrogen bond formation between the two chains, which is believed to represent a form of short-range order in the blend, has been conducted as described in the Experimental Section. These models can in no way be compared to the structures prevailing in the crystal phase, since they cannot be extended to form long-range order. Only two successive hydrogen bonds of *n*I nylons have been considered in this modeling, and the models are proposed to represent a low level of short-range order. Undoubtedly, a large number of conformations will also be present in the disordered regions, as well as hydrogen bond formation between chains of a same polymer. This modeling must therefore be considered as a first attempt at understanding the processes of miscibility at the molecular level through molecular modeling, and the model will certainly need improvement in the future.

The final conformations of the homopolymer models as well as of the two-chain models are given in Table III, and the energy contributions are given in Table IV. These do not include, as stated previously, the stabilizing energy due to the hydrogen bond formation. For the two-chain models, stereoscopic views are given in Figure 8. Two models were studied each time: one with the carbonyl groups of mpI hydrogen bonded to the hydrogen atom of the *n*I nylon, and inversely.

When molecular modeling was used, it was possible to form only one type of hydrogen bond for 5I nylon, between the O atoms of 5I nylon and the H atoms of the amide groups of mpI. It is evident from Figure 8a that, in order to form hydrogen bonds, the 5I nylon has to be in a fully extended conformation. This results in short contacts between the aromatic cycle and the aliphatic chain, and, in order to minimize these, the aromatic cycle adopts a

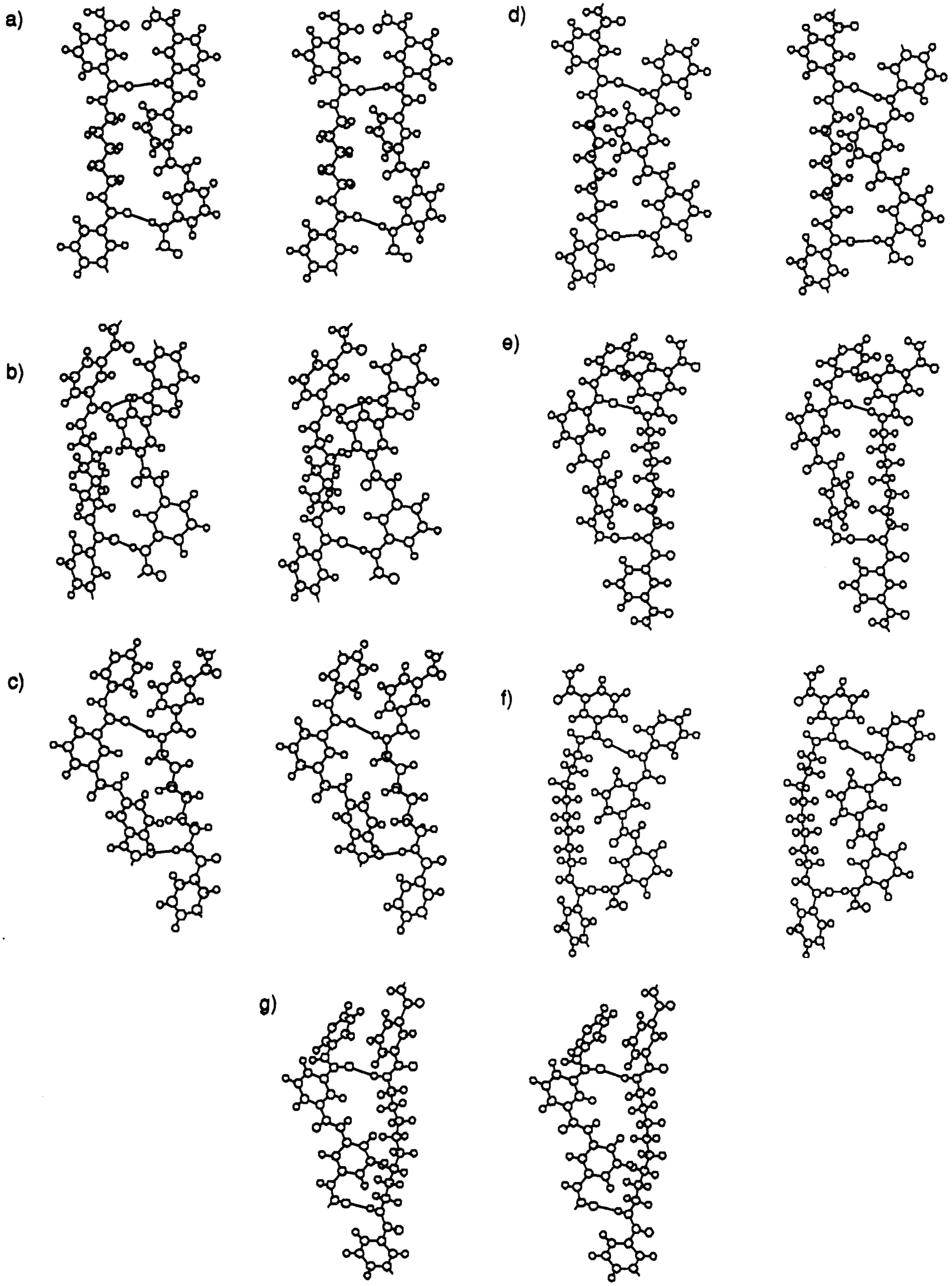


**Figure 8.** Proposed two-chain hydrogen bond formation in blends of *n*I nylon/mpI polymers: (a) 5I nylon/mpI; (b) 6I nylon/mpI, first hydrogen bond scheme; (c) 6I nylon/mpI, second hydrogen scheme; (d) 7I nylon/mpI, first hydrogen bond scheme; (e) 7I nylon/mpI, second hydrogen bond scheme; (f) 8I nylon/mpI, first hydrogen bond scheme; (g) 8I nylon/mpI, second hydrogen bond scheme.

nonplanar conformation, with distortions in the bond distances, bond angles, and torsion angles of the cycle. In spite of this, a 1.82-Å distance is still observed between hydrogen atoms of the two chains. The total energy is consequently significantly higher than those of the other polymer pairs. Hydrogen bond formation between the mpI polyamide and 5I nylon is therefore highly unlikely, and immiscibility results from this.

For the 6I, 7I, and 8I nylons, it was possible to build models having energies comparable to that of the mpI homopolymer but approximately 10 kcal mol$^{-1}$ higher than those of the *n*I nylons. This difference is greater for the nylon 8I/mpI blend, which only exhibits partial miscibility. The energy differences are proposed to be related to the limited miscibility of the 8I nylons as well as to the negative values of the $q$ parameter for the $T_g$–composition relationship, although flexibility of the chains might also play a significant role. No high tensions are observed in the two-chain models, although the $\epsilon$ torsion angles tend to show greater variations than those observed for model compounds of *n*T nylons or predicted from energy considerations. This may be an artifact related to the values of the parameters fixing the energy of the hydrogen bond, which have been given tentatively the same magnitude as those of sp$^3$–sp$^3$ carbon bonds, resulting in a hydrogen bond geometry much more constrained than what is found for the model compounds (H···O distances vary only from 2.068 to 2.083 Å as compared with 1.92 to 2.14 Å for model compounds of *n*T nylons, O–H···N bond angles from 159.5° to 164.9° as compared with 147° to 170°, and C–O···N bond angles from 152.5° to 161.1° as compared with 125.5° to 166°). The constraint on the hydrogen bond geometry is likely to have resulted in deviations of the $\epsilon$ torsion angles, for which the energy barrier was less severe. A better parametrization would be necessary to alleviate such an effect.

Another possible cause is the presence, in the model, of an amide group of mpI that is not hydrogen bonded to another molecule. This amide group is expected to bond with a third chain, either a mpI chain or a *n*I nylon chain. However, in this modeling, in order to simplify the model, this third chain has not been included. Consequently, the amide group might have a tendency to align toward the aliphatic chain of the *n*I nylon in order to form van der Waals contacts, which should not be possible since the amide group must be free to to form hydrogen bonds with another chain.

Short contacts are in both cases related to the presence of $\epsilon$ torsions angles close to 0° or 180°, which results in interactions between the hydrogen and oxygen atoms of the amide group and the ortho hydrogen of the aromatic cycle.

The two-chain models can be used to assess the possibility of complex formation in the crystalline state. For the *n*I nylon/mpI pairs, the irregularity of the hydrogen-bonding pairs is such that this type of complexation is highly unlikely: the conformations leading to hydrogen bonds between the oxygen atoms of mpI and hydrogen atoms of *n*I nylons are very distinct from those leading to hydrogen bonds between hydrogen atoms of mpI and oxygen atoms of the *n*I nylon. Further, the interamide distances leading to the two different hydrogen bond formations are also different.

In summary, the nonmiscibility of the 5I nylon can be related to the impossibility of the 5I nylon chain to form successive hydrogen bonds with the mpI. The miscibility of 6I and 7I nylons has been related to the formation of such bonds, whereas for 8I nylon, although the molecular modeling has proved the possibility of hydrogen bond formation, only partial miscibility has been observed experimentally. This may be related to the higher energy difference calculated for the blend models. It could also be attributed to differences in the number of hydrogen bond forming atoms in the repeat units of the polymers, which could be related to the hydrogen-bonding energy and which has not been included in the calculation. More work is necessary to define parameters that would permit a better evaluation of the conformations and energy of molecules containing hydrogen-bonding atoms.

## Conclusion

At the moment, there is no satisfactory method to predict miscibility, in the literature, or to predict accurately the miscibility of the system studied here. A correlation has been noted between the number of hydrogen bond forming atoms per number of non-hydrogen atoms in the repeat unit of the polymers and miscibility occurrence, although there is not enough information available at this moment to ascertain this relationship. It has been proposed as a rule of thumb to determine possible miscible blends, in particular for systems for which the $\chi$ parameters are not known. This observation has been tentatively proposed to be related to the total hydrogen bond energy of the polymer chains.

A correlation has been established between the amide–amide distances of each polymer in the blend and the miscibility, although these calculations require knowledge of the flexibility of the molecular chains.

Molecular modeling has been used to verify the possibility of hydrogen bond formation of two chains of homopolymers. The results of this study indicate that this approach might be used for miscibility prediction for blends where each of the two homopolymer forms strong self-association. For these polymers, the formation of interchain hydrogen bonds is believed to be mandatory for miscibility occurrence, and the prediction of the possibility of formation of such bonds is therefore proposed to be related to the miscibility behavior of the blends. The results of the present study also suggest a relationship between the difference in energy of the homopolymer pairs and blended pairs and the $T_g$–composition behavior.

At this point, it is necessary to improve the description of hydrogen bond energy parameters, in order to obtain reliable energy values. Further work is also necessary to test the predictive possibilities on more flexible systems and to investigate the other parameters that influence the formation of miscible pairs in such strongly interacting polymers.

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**Registry No.** 3I Nylon (copolymer), 130934-29-1; 3I nylon (SRU), 119495-33-9; 4I nylon (copolymer), 35885-42-8; 4I nylon (SRU), 28757-32-6; 5I nylon (copolymer), 130491-44-0; 5I nylon (SRU), 119495-34-0; 6I nylon (copolymer), 25722-07-0; 6I nylon (SRU), 25668-34-2; 7I nylon (copolymer), 29294-22-2; 7I nylon (SRU), 32008-68-7; 8I nylon (copolymer), 25988-35-6; 8I nylon (SRU), 25950-52-1; 9I nylon (copolymer), 130491-35-9; 9I nylon (SRU), 119495-35-1; 10I nylon (copolymer), 35885-43-9; 10I nylon (SRU), 28883-72-9; mpI (copolymer), 25035-33-0; mpI (SRU), 24938-60-1.