*Macromolecules* **1996,** *29,* 1839−1841

# Factors Affecting the Miscibility of Nylon-6I/Nylon-6,6

**J. Brisson* and P. Côté**

*Centre de Recherche en Sciences et Ingénierie des Macromolécules (CERSIM), Département de Chimie, Faculté des Sciences et de Génie, Université Laval, Québec, Québec, Canada G1K 7P4*

*Received September 28, 1995*
*Revised Manuscript Received November 15, 1995*

In a recent paper, we reported the miscibility behavior of a series of polyamide blends.[1] Some of our conclusions were in disagreement with previous work by Ellis and with a theory proposed in the literature.[2] In a more recent article, Ellis concludes that inappropriate preparation methods and procedures were used to prepare our samples.[3] In the present paper, some additional experiments will be reported to shed light on the specific matter of the miscibility of nylon-6,6,/nylon-6I and related blends and therefore to show that this conclusion was premature.

**Experimental Section.** Synthesis, characterization, and blending of the polymers discussed here have, for most part, been reported previously.[1] In order to avoid turbid solutions when using trifluoroacetic acid, freshly distilled solvent is used and further dried over $MgSO_4$ prior to use. In cases where turbid solutions were obtained, water was added drop by drop until the turbidity disappeared, which usually requires less than 5% water. Blends containing 50% nylon-6,6 and 50% nylon-6I were also prepared by precipitation of a trifluoroethanol/chloroform solution in diethyl ether in exactly the same manner as described in ref 3. DSC measurements of the blends prepared using trifluoroacetic acid are described in ref 1. In the case of the $H_2SO_4$ solutions, DSC scans were performed in a similar manner, at the same heating rate (20 °C/min), but on a Perkin-Elmer DSC-4. Finally, for the trifluoroethanol/$CHCl_3$ solvent, the DSC measurements were performed on a Perkin-Elmer DSC-7, again at the same heating rate.

**Results and Discussion.** The choice of preparation method for nylon blends is a delicate matter. Melt blending was excluded because of thermal degradation problems and transamidation reactions. Solution casting is well known to induce, in some instances, solvent-driven phase separation in thermodynamically miscible blends. Solution precipitation may not be immune to this problem. Different solvent systems were consequently used, as much as possible, to assess miscibility. However, the number of common solvents for nylon blends is severely limited.

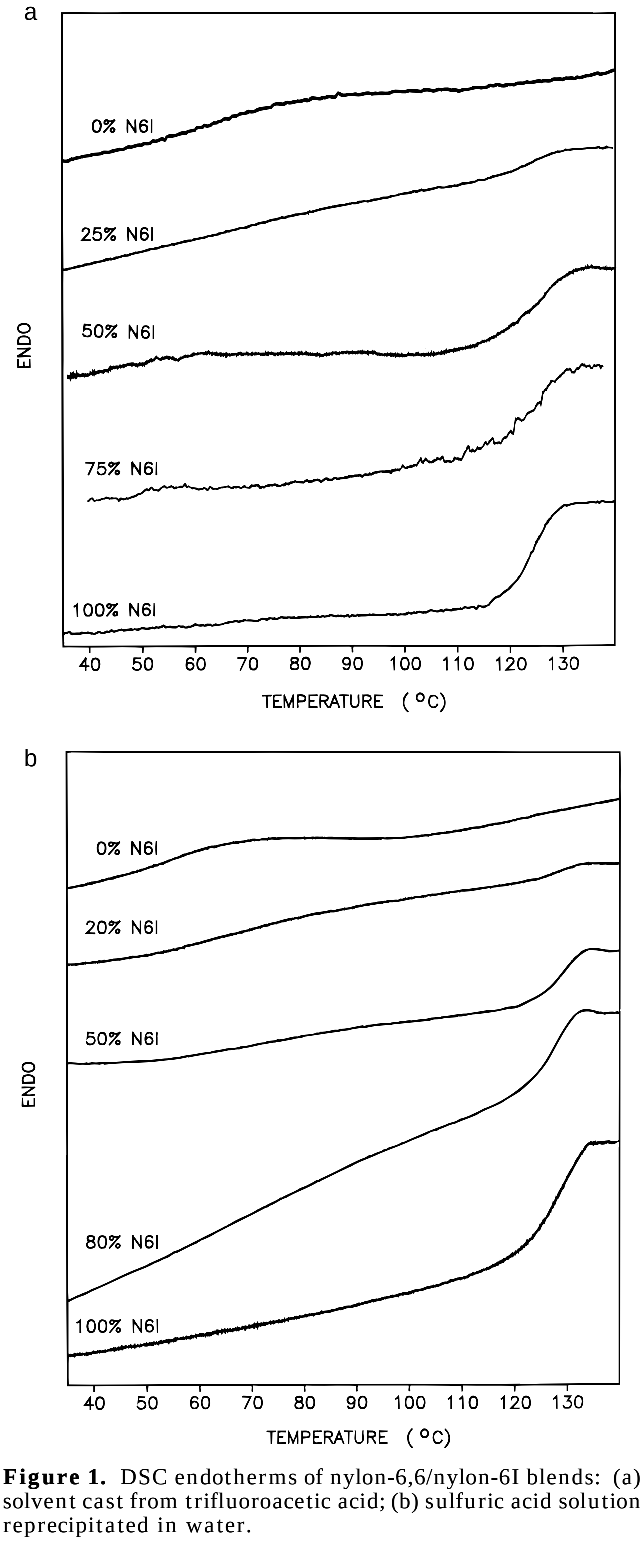

**Figure 1.** DSC endotherms of nylon-6,6/nylon-6I blends: (a) solvent cast from trifluoroacetic acid; (b) sulfuric acid solution reprecipitated in water.

A series of nylons-*n*I/nylon-6,6 blends were prepared for $n = 3-9$ using the sulfuric acid/water precipitant method. Immiscibility was observed for all blends at the concentrations studied (20, 50, and 80% w/w). Since only one solvent system was used, no definite conclusion can be drawn on these systems, which is why these systems have not been included in a full article. However, for $n = 6$, the observed immiscibility was a confirmation of the phase behavior observed using the trifluoroacetic acid solvent, as reported previously.[1] The DSC spectra of the nylon-6,6/nylon-6I blends appear in Figure 1 for both solvent systems. No corrections were made for crystallinity, and only the overall composition is reported. Therefore, since crystallinity can differ, even for the same overall composition, heat capacity jump variations were observed with the solvent system used. In all cases, a glass transition is observed near 125 °C, which is the position of the glass transition of pure nylon-6I. It was usually possible to detect the heat capacity change related to the $T_g$ of nylon-6,6 although this was much more difficult due to the higher crystallinity on nylon-6,6. Nevertheless, the combination of the absence of a glass transition between those of the pure polymers and the appearance of a clearly defined

---

* To whom correspondence should be addressed.

0024-9297/96/2229-1839$12.00/0

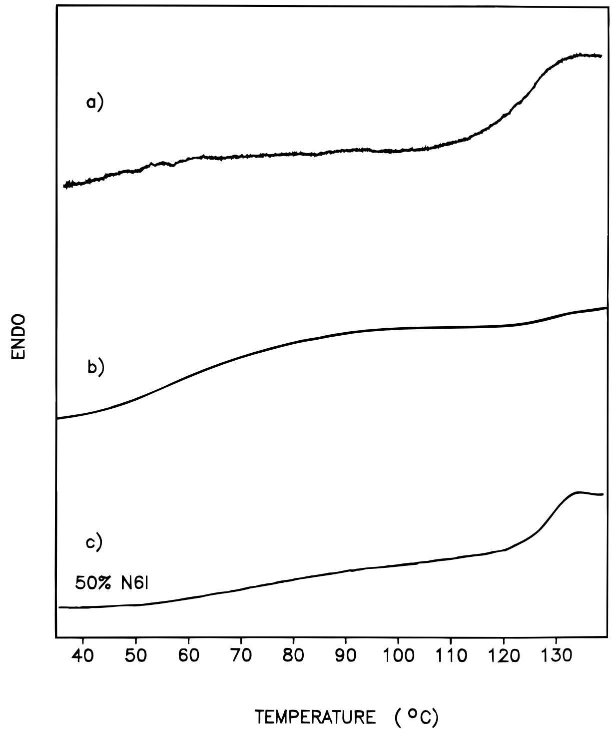

**Figure 2.** DSC endotherms of nylon-6,6/nylon-6I 50% w/w blend: (a) solvent cast from trifluoroacetic acid; (b) trifluoroethanol/chloroform solution reprecipitated in diethyl ether; (c) sulfuric acid solution reprecipitated in water.

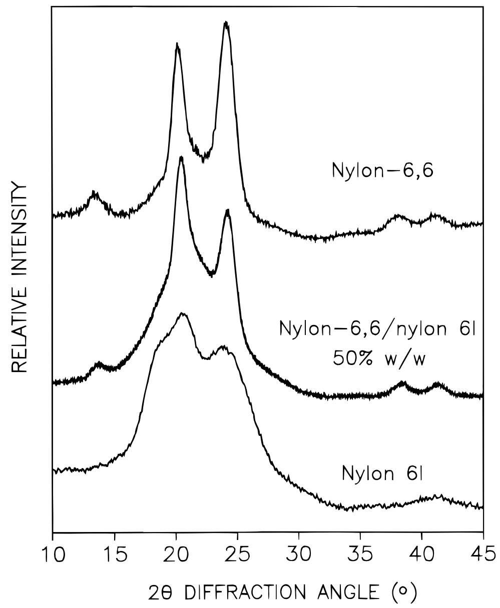

**Figure 3.** X-ray diffraction spectra of crystalline nylon-6,6 (film cast from trifluoroacetic acid solution), crystalline nylon-6I (film recrystallized using methanol), and nylon-6,6/nylon-6I 50% w/w blend prepared using trifluoroethanol solution.

glass transition for nylon-6I are unambiguous indications of the immiscibility of the blends in both solvent systems.

Heating at 280 °C (above the melting point of both polymers), followed by rapid quenching with liquid nitrogen, did not alter the immiscibility of the systems. Crystallinity was drastically reduced at first, although the nylon-6,6 did recrystallize in a matter of hours. The behavior observed here is quite different from that reported by Ellis, who reports an apparent phase-separated system upon the first run. After melting, however, he observes a single glass transition.

In order to better understand this sytem, and to eliminate any uncertainty, a third solvent system was also used for the 50:50 nylon-6,6/nylon-6I blend composition. This solvent, trifluoroethanol/chloroform, was the one advocated as the most suitable by Ellis.[3] In our preliminary studies, it had been observed to induce moderate crystallinity in pure nylon-6I samples, similar to that obtained after submitting samples to ethanol.[4] Since blending of two semicrystalline polymers usually yields samples for which thermal transitions are notoriously difficult to observe, its use had not been attempted in our earlier work. In the present work, however, in order to lift any doubt as to the phase behavior of the polymers used here, a sample having the composition least likely to induce important crystallization, namely a 50:50 blend, was prepared. The DSC scan of this sample is reported in Figure 2, along with those obtained for the two other solvent systems. As can be seen, a slight deviation can be observed around 120 °C, which corresponds to the $T_g$ of the amorphous fraction of nylon-6I. The heat capacity jump associated with the $T_g$ of nylon-6,6 is, in this case, much larger than that of nylon-6I, which is highly unusual and which made us suspect that the nylon 6I was semicrystalline even at this phase composition. The width of the transitions was not, however, significantly different from those of other samples. No intermediate $T_g$ is observed. Melting around 280 °C did not alter this behavior, nor did it alter significantly the crystallinity of the aliphatic nylon.

The DSC scan of the blend was not conclusive with regard to the crystallinity of nylon-6I, since it melts in the form of a large endotherm ranging from 210 to 240 °C, which makes it hard to distinguish from that of nylon-6,6, since the latter presents an asymmetrical endotherm with a first peak starting to appear at ca. 245 °C, followed by the major, sharper peak at 260 °C. The X-ray diffraction scan of this sample is reported in Figure 3, along with the X-ray diffraction spectra of crystalline nylon-6,6 (film obtained by evaporation of a trifluoroacetic acid film) and nylon-6I (crystallized using methanol as in ref 4). Since the major diffraction peaks of the two polymer phases are mostly superimposed, evaluation of the composition is difficult. However, it is clear that the major crystalline phase present is that of nylon-6,6. A shoulder at 18° is attributed to the nylon-6I crystal phase.

The first conclusion that is reached from this reappraisal is that, contrarily to what is proposed by Ellis, the trifluoroethanol−chloroform solvent suffers from some drawbacks, since it favors crystallization of nylon-6I. The sulfuric acid system, in theory, is therefore the best one. Unfortunately, it cannot be used to prepare films. Trifluoroacetic acid is a difficult solvent to use, can lead to phase-separated systems if care is not taken to control water content, and requires extremely long drying times if high temperatures are to be avoided. However, it is still a viable option, provided verifications are made, either by melting the polymers for a short time or by using a sulfuric acid solutions reprecipitated in water.

More interesting is the reason behind the different behavior observed in the two independent studies. In particular, the occurrence of crystallization of nylon-6I when using the trifluoroethanol solvent in the present work, coupled with the statement made by Ellis that the nylon-6I he used was an amorphous polymer, clearly points to structural differences between the two polymers. It has long been known that nylon-6I is a semicrystalline polymer.[5] Indeed, although nylons-*n*I crystallize with much more difficulty than most other nylons, conditions under which they do crystallize have been reported.[4,5] It is well known that structural regularity is required for crystallization to proceed. The use of two different synthetic methods may have caused sufficient structural changes to alter the crystallization ability of the polymer. Polymers used here were obtained through interfacial polycondensation, which gives regular polymers of high polydispersity. Commercial nylons of the type used by Ellis are usually synthesized by melt polycondensation. At high temperatures, some branching is liable to occur. This could result in a less regular polymer, and therefore is a polymer which crystallizes less readily. Differences in end groups, molecular weights, or distributions could also be invoked to explain these observations. However, end groups usually have little effect on the crystallinity, whereas molecular weights or distributions, in this case, should favor the crystallization of the melt polycondensation product, which is clearly not the case. In all events, the fact that such synthesis-related structural differences may affect miscibility is a surprising, albeit extremely interesting possibility.

The present observation could also support the distinction between copolymers and homopolymers in blend behavior. If one accepts that interaction formation drives miscibility, then any change in interaction formation is likely to alter miscibility. Copolymers, and particularly random copolymers, exhibit behaviors which are often drastically different from their parent polymers, as demonstrated by their solubility, crystallinity, and thermal behavior. These differences are related to changes in the ability to form specific interactions with given molecules. Conceptually and physically, homopolymers and copolymers differ in their interactions with their environment.

Predicting miscibility implies predicting interaction formation. The binary interaction model (BIM) and the rule of thumb we previously proposed are different approximations to this problem, each bearing intrinsic limitations which influence their usefulness. In order to achieve better predictions of the miscibility, one needs to predict as accurately as possible interaction formation. Molecular modeling has the ability to take into account fine structural details such as tacticity and limited cross-linking. Qualitative approaches of the type used previously in our group[7] are fast being replaced with statistically significant averaging techniques.[8] With the advent of better computational facilities and with future advances in modeling techniques, it can be surmised that they will not only provide an alternate route to miscibility prediction but also help unravel the relative importance of the various factors influencing, when not controlling, miscibility.

**Conclusion.** Although, as Ellis states, 'it is possible to derive erroneous assessment of phase behavior if inappropriate preparative and analytical procedures are followed', it is shown here that this was not the case in our previous study. Neither our previous paper[1] nor that of Ellis[2] are believed to be in error, the discrepancy being most probably due to differences in polymer structure or polydispersity. This illustrates how important, when comparing miscibility results, the choice of the polymer source and the investigation of possible, often overlooked structural differences can be.

**Acknowledgment.** The authors would like to acknowledge the work of Marie-Claude Guimond, who prepared the nylon-*n*,*m*/nylon-6I blends using sulfuric acid, and that of Sylvie Plante, who was responsible for the results reported for the nylon-6,6/nylon-*n*I blends. We would also like to acknowledge the financial support of NSERC.

## References and Notes

(1) Côté, P.; Brisson, J. *Macromolecules* **1994**, *37*, 7329.
(2) Ellis, T. S. *Macromolecules* **1991**, *24*, 3845.
(3) Ellis, T. S. *Macromolecules* **1996**, *29*, 1836.
(4) Liu, W.; Brisson, J. *J. Polym. Sci., Polym. Phys. Ed.* **1995**, *33*, 619.
(5) Brisson, J.; Breault, B. *Macromolecules* **1991**, *24*, 495.
(6) Kotliar, A. M. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1978**, *19* (2), 111.
(7) Bonner, W. H. *U.S. Patent* 3,088,794, 1963.
(8) Tiller, A. P.; Gorella, B. *Polymer* **1994**, *15*, 3251.

MA951472E