Transamidation in Melt-Mixed Aliphatic and Aromatic Polyamides. 2. Molecular Characterization of PA 46/PA 6I Blends as a Function of the Extrusion Time, Extrusion Temperature, and Blend Composition

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ABSTRACT: The structure of polyamide 46/polyamide 6I copolymers obtained by reaction in the molten state is analyzed as a function of the extrusion time, the extrusion temperature, and the overall blend composition by ^{13}C NMR. The degree of transamidation, the degree of randomness, and the number-average block length of the copolymers are calculated using the method for a four-component polyamide system. It is shown that the transamidation processes are occurring very fast during the first period of melt-mixing but are slowing down at longer extrusion times. High extrusion temperatures affect the transamidation processes in an increasing way. From ^{13}C NMR experiments on PA 46/PA 6I copolymers with different compositions, differences in reactivities are observed. The change of the molecular structure of the copolyamides as a function of the processing conditions and the overall blend composition strongly affects their crystallization behavior.

Introduction

Blends of polycondensates are widely used in a large range of applications. Most popular blend systems in this category of polymer blends are polyester/polyester, polyester/polyamide, and polyamide/polyamide blends. Melt-processing of polycondensates, however, causes reactions to occur between the blend components. The number of these interchange reactions is limited for nonmiscible blend systems because of the small reaction volume at the interface of the two separated phases. In miscible blend systems, the total number of reactions becomes much larger and the impact hereof on the final properties must not be underestimated.

The melt-processing of polycondensates has received a lot of attention in the past, but the studies were most often restricted to the observation of changes in the final properties due to the melt-mixing processes.[1−5] Interesting properties studied were the phase behavior, the crystallization and melting temperatures, and the mechanical behavior. It is however important to have a better insight into the change of the molecular structure of polycondensates due to the occurrence of transreaction processes in order to understand the final properties. A change of molecular structure will often define a new morphology, with possible implications for the final properties of the blends.

Transesterification reactions in some polyester blend systems have been studied in the past by NMR or FTIR measurements.[6−11] The present paper describes the change of the molecular structure of polyamides due to transamidation reactions occurring during the melt-mixing process of a miscible PA 46/PA 6I blend system.

It has already been shown in a previous paper how transamidation reactions can affect the thermal properties of PA 46/PA 6I blends such as the crystallization and the melting behavior.[12,13] This was ascribed to the transformation of the homopolyamides into block copolyamides with crystallizable and amorphous block sequences. It was investigated to what extent the extrusion temperature, the extrusion time, and the overall blend composition affect the thermal properties of the copolyamides formed.

In the study of the relation melt processing−molecular structure−thermal properties, it will be investigated how the melt-processing conditions and the blend composition determine the molecular structure of the copolymers formed and their resulting crystallization and melting behavior. In this respect, it is very important to know the average length of the homologous blocks of the aliphatic polyamide 46 in the copolyamide as a function of the processing conditions; this can give interesting information with respect to the kinetics and the ability of crystallization.

In the accompanying paper, high-resolution nuclear magnetic resonance (NMR) was used, and in particular ^{13}C NMR, as an effective tool for the determination of the sequence distribution in aliphatic/aromatic copolyamides.[14] It was observed that the carbonyl signal resonances of the copolyamides are sensitive to diad sequence distributions. Using a statistical model, the average copolymer composition, the number-average block length, the degree of transamidation, and the degree of randomness were computed.

Experimental Section

Blend Materials. See part 1.[14]

Preparation of the Copolyamides. The copolyamides were prepared by melt-mixing the two different homopolyamides (PA 46 and PA 6I) using a minimixer. The following processing conditions were varied: extrusion time, extrusion temperature, and overall blend composition. The various copolyamides, obtained under different processing conditions, are described in Table 1. The molecular weight of the resulting copolyamides was not determined because of the complexity of this.

Calorimetric Measurements. DSC measurements were performed on a Perkin-Elmer Delta Series DSC 7. The samples were first brought to the molten state at 300 °C for 1 min and subsequently cooled to 100 °C at a rate of 10 °C/min. All experiments were performed under a nitrogen atmosphere, and liquid nitrogen was used as cooling agent.

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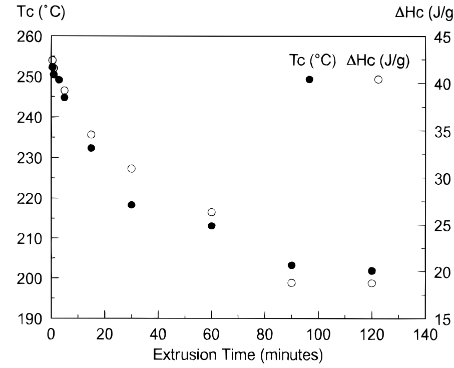

Figure 1. Influence of the extrusion time on the crystallization peak temperature and the crystallization enthalpy of PA 46/PA 6I blends (50/50) (w/w) during the slow cooling from the melt (10 °C/min). Extrusion temperature: 315 °C.

Table 1. Series of PA 46/PA 6I Blend Compositions with Different Melt-Mixing Conditions

blend	blend comp (PA46/PA6I)	extrusion time (min)	extrusion temp (°C)
A	50/50	5	315
B	50/50	15	315
C	50/50	30	315
D	50/50	60	315
E	50/50	90	315
F	50/50	120	315
G	50/50	60	295
H	50/50	60	305
I	50/50	60	315
J	50/50	60	325
K	85/15	90	315
L	70/30	90	315
M	50/50	90	315
N	30/70	90	315
O	15/85	90	315

NMR Measurements. See part 1.[14]

Results and Discussion

Thermal Analysis. The crystallization temperature and the crystallization enthalpy of the PA 46/PA 6I (50/50) blend are plotted in Figure 1 as a function of the extrusion time at 315 °C. The crystallization enthalpy is given in joules per gram of the blend. It can be seen that the crystallization temperature and the crystallization enthalpy are decreasing to a large extent during the first 60 min of the melt-extrusion process. This decrease becomes smaller at higher extrusion times.

The influence of the extrusion temperature on the crystallization temperature and the crystallization enthalpy of the PA 46/PA 6I (50/50) blend is represented in Figure 2; the extrusion time hereby is set at 60 min. It can clearly be seen that the crystallization rate and the crystallization enthalpy are strongly decreasing with increasing extrusion temperature in the temperature range 295−325 °C.

From the above data, it can be concluded that crystallization of PA 46 in the blends becomes more difficult when the polyamide blends are melt-mixed for long extrusion times and at high extrusion temperatures, which was also found in a previous paper.[12] However, the blends composed of 50% PA 46 and 50% PA 6I are still able to crystallize, even after very long melt-mixing times at higher temperatures.

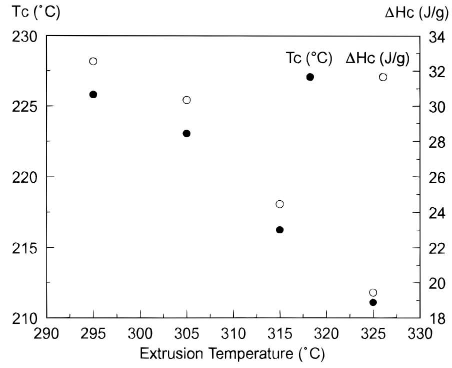

Figure 2. Influence of the extrusion temperature on the crystallization peak temperature and the crystallization enthalpy of PA 46/PA 6I blends (50/50) (w/w) during slow cooling from the melt (10 °C/min). Extrusion time: 60 min.

Table 2. Crystallization Parameters of Different PA 46/PA 6I Blend Compositions after Melt-Mixing for 90 min at 315 °C.

blend	T_c (°C)	ΔH_c (J/g)
K(85/15)	238	55
L(70/30)	228	41
M(50/50)	203	19
N(30/70)		
O(15/85)		

The ability of crystallization can also be affected by changing the blend composition when the melt-mixing conditions are kept constant. Table 2 contains the crystallization and melting data of different blend compositions which were melt-processed for 90 min at 315 °C. The crystallization of PA 46 in the blends becomes more difficult at higher PA 6I contents in the blends. Crystallization is inhibited for the blends consisting of 70% or more PA 6I by weight; this is also confirmed by their transparency at room temperature.

Molecular Characterization. (a) Influence of the Extrusion Time on the Molecular Structure. The ^{13}C NMR spectra of the polyamide blend PA 46/PA 6I (50/50 by weight) processed at 315 °C were recorded as a function of the extrusion time. In Figure 3, the expanded ^{13}C NMR spectra of the carbonyl region of the different copolymers formed are shown. The assignments of the carbonyl resonance signals of the PA 46/PA 6I copolyamide system were made in the accompanying paper and are also indicated in Figure 3.[14]

As can be seen in this figure, the peak intensities of the different diad sequences change as a function of the extrusion time. The peak intensities at 171.71 and 177.62 ppm, i.e., the concentration of diad sequences A_2B_1 and A_1B_2, respectively, increase as a function of the extrusion time, implying a growing number of transamidation reactions. As a consequence, the crystallizable sequences of PA 46 and the amorphous sequences of PA 6I become shorter with increasing melt-mixing time. In Table 3A, the fraction of the diad sequences are tabulated as a function of the extrusion time. The number-average block lengths of the various sequences (x, y, z and w), the degree of transamidation ψ, the degree of randomness χ, and the values for m and n are listed in Table 3B. All the results are compared with the theoretical values of an unreacted PA 46/PA 6I blend (physical blend) and a fully random copolymer of the same composition (x is the block length of the A_1B_1 diad, and y, z, and w are the block lengths of the diads A_1B_2, A_2B_1, and A_2B_2, respectively). The corresponding equations are given in the accompanying

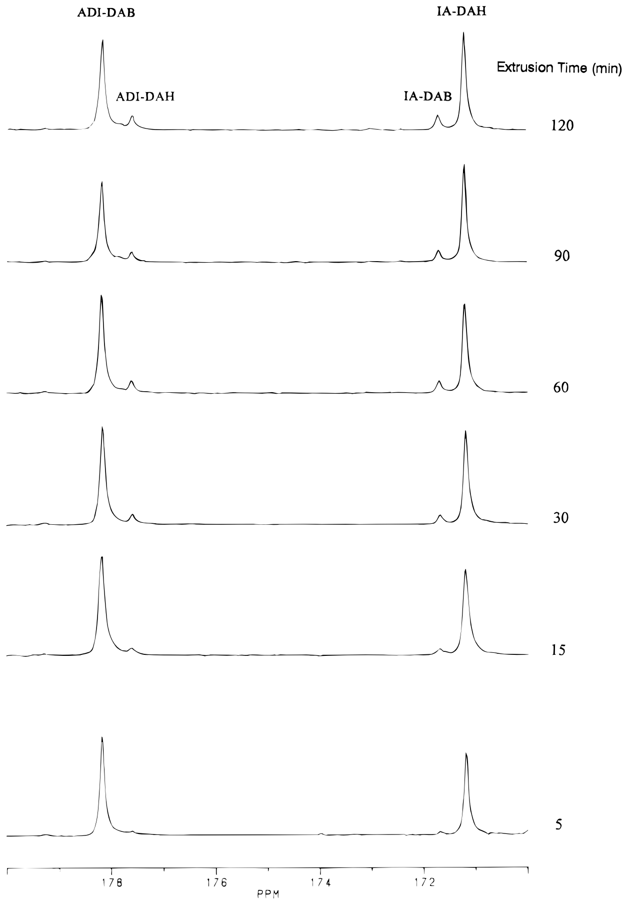

Figure 3. Expanded 62.5 MHz ^{13}C NMR spectra showing only the carbonyl region of a mixture of PA 46 and PA 6I (50/50) processed at 315 °C for different extrusion times. The different extrusion times are indicated in the figure.

Table 3

A. Experimentally Determined Relative Peak Areas of the Carbonyl Carbon of PA 46/PA 6I Copolymers Prepared by Melt-Mixing at 315 °C as a Function of the Extrusion Time (PA46/PA 6I: 50/50 (w/w))

blend	$F(A_1)$	$F(A_2)$	$F(A_1B_1)$	$F(A_1B_2)$	$F(A_2B_2)$	$F(A_2B_1)$
A(5)	0.553	0.447	0.535	0.018	0.426	0.021
B(15)	0.520	0.480	0.493	0.027	0.447	0.033
C(30)	0.518	0.482	0.470	0.048	0.427	0.055
D(60)	0.527	0.473	0.469	0.057	0.411	0.062
E(90)	0.484	0.516	0.423	0.060	0.455	0.061
F(120)	0.498	0.502	0.430	0.068	0.426	0.076
physical blend[a]	0.500	0.500	0.500	0	0.500	0
random copolym[b]	0.500	0.500	0.250	0.250	0.250	0.250

B. Calculated Number-Average Sequence Lengths, Degree of Transadmidation and Degree of Randomness for PA 46/PA 6I Copolymers Prepared by Melt-Mixing at 315 °C as a Function of the Extrusion Time (PA46/PA 6I: 50/50 (w/w))

blend	x	y	z	w	m	n	ψ	χ
A(5)	30.72	1.03	1.05	21.28	2.45	4.63	3.90	0.07
B(15)	19.26	1.05	1.07	14.54	3.54	6.99	6.00	0.11
C(30)	10.71	1.10	1.13	8.83	6.06	10.99	10.30	0.19
D(60)	9.17	1.12	1.15	7.64	7.09	12.29	11.94	0.23
E(90)	8.01	1.14	1.13	8.44	7.18	12.04	12.16	0.24
F(120)	7.27	1.16	1.18	6.61	8.07	14.50	14.44	0.27
physical blend[a]	104	0	0	36			0	0
random copolym[b]	2.00	2.00	2.00	2.00	17.10	28.14	50.00	1.00

[a] Physical mixture of the two homopolymers PA 46 and PA 6I.
[b] Hypothetical random copolymer of PA 46/PA 6I.

paper.[14] At low degrees of transamidation, the quantification of the different relative diad concentrations will be less accurate, i.e., for copolymers prepared by extrusion times shorter than 15 min.

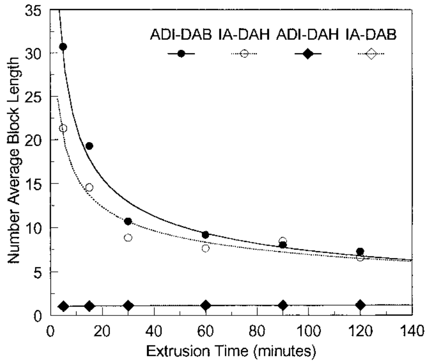

Figure 4. Number-average block lengths of the various sequences as a function of the extrusion time (blend composition: 50/50 (w/w) PA 46/PA 6I; extrusion temperature: 315 °C).

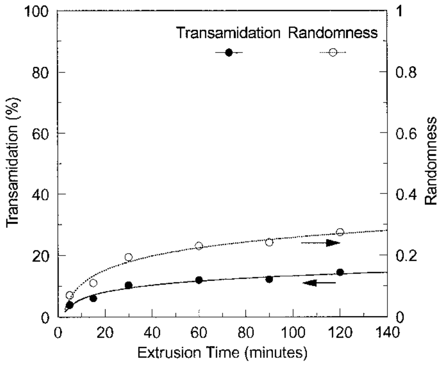

Figure 5. Degree of transamidation and degree of randomness as a function of the extrusion time (blend composition: 50/50 (w/w) PA 46/PA 6I; extrusion temperature: 315 °C).

In Figure 4, the number-average block lengths of the various sequences are plotted against the melt-mixing time. It can be seen that the average block length of PA 46, i.e., homologous groups consisting of A_1B_1 next to each other, decreases to 7 after melt-mixing for 120 min at 315 °C. This is obviously still long enough to allow crystallization (see previous section). The length of the amorphous PA 6I blocks decreases in a similar way as for PA 46. Figure 5 represents the degree of transamidation and the degree of randomness as a function of the extrusion time at 315 °C. The highest value of transamidation obtained by melt-mixing for 120 min at 315 °C is 14%, which means that 14% of the polyamide bonds of the two blend components PA 46 and PA 6I (A_1B_1 and A_2B_2) have been converted into new polyamide bonds A_1B_2 and A_2B_1. This corresponds to a degree of randomness of 0.27. A fully random copolymer would have a degree of transamidation of 50% and the χ-value would be 1. An alternating copolyamide would have a degree of transamidation of 100% and χ would be 2. It is clear from the above-mentioned data and especially from the χ-values that the melt-processed copolymers still have a block character, which explains their ability to crystallize. From these results, it is also obvious that the transamidation reactions in the melt do not readily provide a practical method for preparing high molecular weight random copolyamides starting from high molecular weight homopolyamides. A similar conclusion was drawn by Beste and Houtz[15] in their study of amide interchange reactions between sebacamide and *N*,*N*′-diacetylhexamethylenediamine.

Table 4

A. Experimentally Determined Relative Peak Areas of the Carbonyl Carbon of PA 46/PA 6I Copolymers Prepared by Melt-Mixing during 60 min as a Function of the Extrusion Temperature (PA 46/PA 6I: 50/50 (w/w))

blend	$F(A_1)$	$F(A_2)$	$F(A_1B_1)$	$F(A_1B_2)$	$F(A_2B_2)$	$F(A_2B_1)$
G(295)	0.533	0.467	0.486	0.047	0.416	0.051
H(305)	0.536	0.464	0.483	0.053	0.413	0.051
I(315)	0.510	0.490	0.450	0.059	0.436	0.054
J(325)	0.512	0.488	0.442	0.071	0.412	0.075
physical blend[a]	0.500	0.500	0.500	0	0.500	0
random copolym[b]	0.500	0.500	0.250	0.250	0.250	0.250

B. Calculated Number-Average Sequence Lengths, Degree of Transamidation, and Degree of Randomness for PA 46/PA 6I Copolymers Prepared by Melt-Mixing during 60 min as a Function of the Extrusion Temperature (PA 46/PA 6I: 50/50 (w/w))

blend	x	y	z	w	m	n	ψ	χ
G(295)	11.42	1.10	1.12	9.16	5.92	10.40	9.77	0.19
H(305)	10.13	1.10	1.12	9.04	6.63	10.47	10.42	0.21
I(315)	8.59	1.13	1.12	9.08	7.20	10.87	11.33	0.24
J(325)	7.27	1.16	1.18	6.49	8.37	14.39	14.56	0.28
physical blend[a]	104	0	0	36			0	0
random copolym[b]	2.00	2.00	2.00	2.00	17.10	28.14	50.00	1.00

[a] Physical mixture of the two homopolymers PA 46 and PA 6I.
[b] Hypothetical random copolymer of PA 46/PA 6I.

(b) Influence of the Extrusion Temperature on the Molecular Structure. Melt-mixing of PA 46/PA 6I blends for a constant blending period but at varying extrusion temperatures will give rise to a different chain microstructure for the resulting copolymers. Table 4A gives the fraction of diad sequences as a function of the extrusion temperature. In Table 4B, the experimental value of the average sequence lengths of PA 46 and PA 6I, the degree of transamidation, and the degree of randomness are tabulated as a function of the extrusion temperature. It can be seen that the block length of PA 46 in the copolymer formed decreases with increasing extrusion temperature. This explains the decreasing crystallization temperature during a controlled DSC cooling experiment with increasing extrusion temperature as shown in Figure 2; the crystallization will be more difficult, which is also reflected by a lowering of the crystallization enthalpy. Increasing the melt-mixing temperature raises the degree of transamidation from about 10% for melt-mixing at 295 °C to about 14.5% when the blends are extruded at 325 °C. The degree of randomness is increased under the previous circumstances from 0.19 to 0.28. With the information described above, one can reach a certain degree of transamidation either by performing melt-mixing for short periods at high temperatures or by melt-mixing for long periods at lower temperatures. This is illustrated by the next example; if one attempts, for instance, to reach a block length of 7 A_1B_1 units of PA 46 next to each other in the copolymer, which corresponds to a block length of 102.9 Å, it can be done either by melt-mixing PA 46 and PA 6I (50% each by weight) for 120 min at 315 °C or by melt-mixing the same blend composition for 60 min at 325 °C. In both methods, the degree of transamidation will be 14.5% and the degree of randomness 0.27−0.28. However, the obtained copolymers are still far from random.

(c) Influence of the Blend Composition on the Molecular Structure. The block sequence distribution of PA 46 and PA 6I in copolyamides, obtained by reactive extrusion, changes dramatically if the overall starting blend composition is changed. In Figure 6, the recorded ^{13}C NMR spectra are plotted as a function of the blend composition. The peak intensities at 171.21 and 178.20 ppm vary depending on the overall blend composition. However, it can also be seen that the peak intensities at 171.71 and 177.62 ppm, which represent the concentration of A_2B_1 and A_1B_2, respectively, are clearly changing with increasing weight content of PA 6I. Figure 7 shows the resulting block lengths of PA 46 and PA 6I after melt-mixing the blends for 90 min at 315 °C. The homogeneous blocks of the PA 46 sequences A_1B_1 decrease from 30.5 for the blend composition 85/15 (w/w) PA 46/PA 6I to 2 for the blend composition 15/85 (w/w) PA 46/PA 6I. The PA 46 block

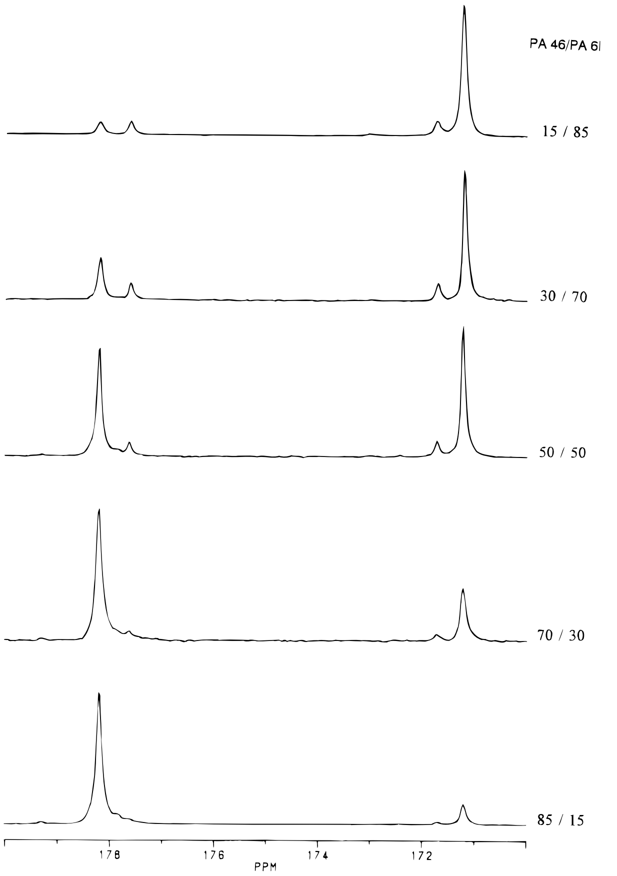

Figure 6. Expanded 62.5 MHz ^{13}C NMR spectra showing the carbonyl region only of mixtures of PA 46 and PA 6I for different blend compositions (processing temperature: 315 °C; extrusion time: 90 min). The different blend compositions by weight are indicated in the figure.

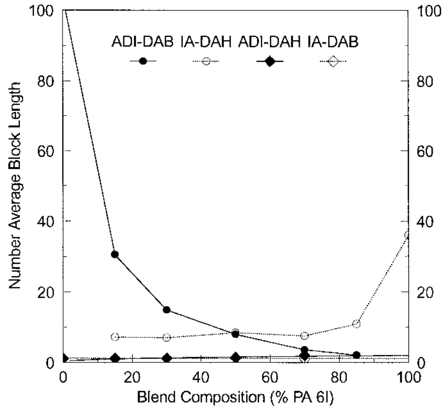

Figure 7. Number-average block length of the various sequences as a function of the blend composition (extrusion temperature: 315 °C; extrusion time: 90 min).

Table 5

A. Experimentally Determined Relative Peak Areas of the Carbonyl Carbon of PA 46/PA 6I Copolymers Prepared by Melt-Mixing during 90 min at 315 °C as a Function of the Blend Composition

blend	$F(A_1)$	$F(A_2)$	$F(A_1B_1)$	$F(A_1B_2)$	$F(A_2B_2)$	$F(A_2B_1)$
K(85/15)	0.856	0.144	0.827	0.028	0.124	0.020
L(70/30)	0.696	0.304	0.650	0.047	0.261	0.043
M(50/50)	0.484	0.516	0.423	0.060	0.455	0.061
N(30/70)	0.311	0.689	0.225	0.086	0.597	0.092
O(15/85)	0.149	0.851	0.075	0.074	0.773	0.078

B. Calculated Number-Average Sequence Lengths, Degree of Transamidation, and Degree of Randomness for PA 46/PA 6I Copolymers Prepared by Melt-Mixing during 90 min at 315 °C as a Function of the Blend Composition

blend	x	y	z	w	m	n	ψ	χ
K(85/15)	30.54	1.03	1.16	7.20	4.49	4.68	4.80	0.23
L(70/30)	14.90	1.07	1.16	7.06	6.60	9.19	8.97	0.22
M(50/50)	8.00	1.14	1.13	8.44	7.18	12.04	12.16	0.24
N(30/70)	3.60	1.38	1.15	7.52	7.81	16.37	17.79	0.40
O(15/85)	2.01	1.99	1.10	10.91	4.35	13.62	15.20	0.58

length after melt-extrusion of 30% PA 46 and 70% PA 6I numbers 3.6, corresponding to a block length of 52.9 Å, which is obviously too small to retain the ability to crystallize. This explains the failure of crystallization for the latter blend composition, as was already observed in the section on thermal analysis (see Table 2).

From a statistical point of view, one would expect that the sequence length of PA 6I would decrease in a similar way by adding PA 46 to PA 6I. However, the block length of PA 6I drops from 36 A_2B_2 units to 11 by adding only 15% of PA 46 to PA 6I. A further decrease in the sequence length of PA 6I is rather small at higher weight contents of PA 46 (see Table 5B). The difference in decrease of block sequence lengths of both PA 46 and PA 6I as a function of blend composition can only be explained by a difference in reactivity between PA 46 and PA 6I or by the presence of catalyst in PA 6I. However, no traces of catalyst were found in either of the blend components, not even on a ppm scale. In Figure 8, the degree of randomness and the degree of transamidation are plotted as a function of the blend composition. Also here, it can be noticed that the degree of randomness, which is by definition independent of the blend composition, increases with increasing weight content of PA 6I. The data of several blend compositions are tabulated in Table 5. From a statistical point of view, it would be expected that the degree of transamidation reaches a maximum at a 50/50 PA 46/PA 6I ratio. Instead, the maximum has shifted to a higher content of PA 6I (about 70% PA 6I). All these observations indicate a higher reactivity of the blends which contain a large weight fraction of PA 6I. The reason why is unknown at this time and further investigation is needed.

Conclusions

The ability of PA 46 to crystallize in a melt-mixed blend with PA 6I is affected by exchange reactions which take place during melt-processing. Increasing the extrusion temperature, the extrusion time, and the weight content of PA 6I in the blends decreases the crystallization ability of PA 46 in the blend. A full characterization of the molecular structure of the PA 46/PA 6I copolyamdies after melt-extrusion reveals a decreasing block length of PA 46 when the extrusion temperature and the extrusion time are raised. This explains the decrease of the crystallization temperature during cooling from the melt and the crystallization enthalpy of PA 46 in the blends. However, the copolymers resulting from blends composed of 50% PA 46 and 50% PA 6I are still far from random, which implies that the number-average block lengths are still long enough to allow crystallization, even after melt-mixing for long extrusion times at high extrusion temperatures. The shortest block length which was attained in this work for the blend composition 50/50 PA 46/PA 6I was a crystallizable block length of 7.27.

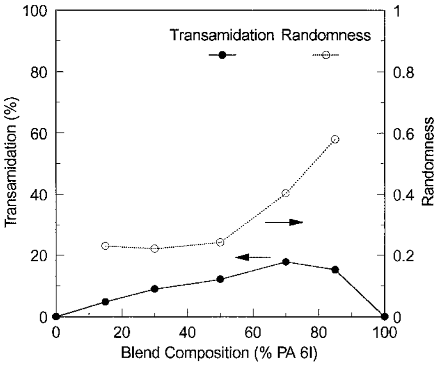

Figure 8. Degree of transamidation and degree of randomness as a function of the blend composition (extrusion temperature: 315 °C; extrusion time: 90 min).

It is also observed that increasing the weight content of PA 6I in the blends enhances the exchange reactions between the blend components. Crystallization of the blend can be inhibited by melt-mixing 70% PA 6I with 30% PA 46 for 120 min at 315 °C; the PA 46 block length of 3.5−4 then becomes too small to be able to crystallize.

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References and Notes

(1) Smith, W. A.; Barlow, J. W. Paul, D. R. *J. Appl. Polym. Sci.* **1981**, *26*, 4233.
(2) Kimura, M.; Salee, G.; Porter, R. S. *J. Appl. Polym. Sci.* **1984**, *29*, 1629.
(3) Eguiazábal, J. I.; Cortázar, M.; Iruin, J. J. *J. Appl. Polym. Sci.* **1991**, *42*, 489.
(4) Cortázar, M.; Eguiazábal, J. I.; Iruin, J. J. *Eur. Polym. J.* **1994**, *30*, 901.
(5) Takeda, Y.; Paul, D. R. *Polymer* **1991**, *15*, 2771.
(6) Devaux, J.; Godard, P.; Mercier, J. P. *Polym. Eng. Sci.* **1982**, *22*, 229.
(7) Devaux, J.; Godard, P.; Mercier, J. P. *J. Polym. Eng. Sci., Polym. Phys. Ed.* **1982**, *20*, 1881.
(8) Yamadera, R.; Murano, M. *J. Polym. Sci., Part A-1* **1967**, *5*, 2259.
(9) Miley, D. M.; Runt, J. *Polymer* **1992**, *33*, 4643.
(10) Valero, M.; Iruin, J. J.; Espinosa, E.; Fernández-Berridi, M. J. *Polym. Commun.* **1990**, *31*, 127.
(11) Kricheldorf, H. R. *Makromol. Chem.* **1978**, *179*, 2133.
(12) Eersels, K. L. L.; Groeninckx, G. *Polymer*, accepted.
(13) Eersels, K. L. L.; Groeninckx, G. *J. Appl. Polym. Sci.*, submitted.
(14) Aerdts, A. M.; Eersels, K. L. L.; Groeninckx, G. *Macromolecules* **1996**, *29*, 1041.
(15) Beste, L. F.; Houtz, R. C. *J. Polym. Sci.* **1952**, *8*, 395.

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