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Transamidation in Melt-Mixed Aliphatic and Aromatic Polyamides. 1. Determination of the Degree of Randomness and Number-Average Block Length by Means of ^{13}C NMR

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ABSTRACT: The NMR spectra of polyamide 46/polyamide 6I copolymers, which were obtained by reaction in the molten sate, are studied. Using ^{13}C NMR, a physical blend of polyamide 46 and polyamide 6I and a polyamide 46/polyamide 6I copolymer could be discriminated. Four kinds of diad sequences are observed in the carbonyl resonance signals of the polyamide 46/polyamide 6I copolymer, and an assignment has been made. From the relative peak areas of the diad sequences and using a statistical method for a four-component polyamide system, the degree of transamidation, the degree of randomness, and the number-average block length have been calculated.

Introduction

In the study of transamidation reactions in the molten state of polyamide blends, it is important to know whether the resulting product is actually a block copolymer, a random copolymer, or a mixture of two homopolyamides. In polyamide blends composed of a semicrystalline aliphatic polyamide and an amorphous aromatic polyamide, the knowledge of the block length of the homogeneous blocks of the aliphatic polyamide can give information about the kinetics and the ability of crystallization.[1] It is known that at temperatures of 250 °C, copolymer formation occurs by amide exchange in a melt of two polyamides.[2,3] Some attempts have been made in the literature to characterize the extent of interchange reactions in mixtures of poly(*m*-xylene-adipamide) and nylon 6[4] and also in mixtures of nylon-*xy* polymers,[5] where *x* indicates the number of carbon atoms separating the nitrogen atoms in the diamine, and *y* the number of straight-chain carbon atoms in the dibasic acid. However, these analyses[4,5] by means of proton NMR are not sufficiently convincing, and more results can be obtained as will be shown in this paper.

The determination of the average block length and sequence distribution of the copolyamides resulting from exchange reactions can be performed by means of high-resolution nuclear magnetic resonance (NMR). NMR has been applied in several ways to polyamides as described in three different reviews.[6−8] The first review deals with the application of proton NMR, discussing the assignment of commercially available polyamides,[6] and the second one deals with the application of ^{15}N NMR for the characterization of co- and terpolyamides.[7] The third review is, in our case, the most interesting one and deals with proton and carbon NMR studies of polyamides in solution.[8] In the latter review,[8] the possibilities and limitations of the sequence determination in aliphatic, mixed aliphatic−aromatic, and aromatic copolymers are discussed.

According to the literature, proton NMR has been used as a tool to identify polyamides and copolyamides, but on the basis of the investigation by Kricheldorf et al.,[9] it is concluded that proton NMR is not a general tool for discriminating between aliphatic copolyamides and blends of homopolyamides. Since the pioneering work of Kricheldorf and co-workers,[9−16] it is well known that the shift differences for blends of homopolyamides, alternating copolyamides, and random copolyamides especially occur in the carbon-13 carbonyl region. This is mainly possible when the polyamides are dissolved in sulfuric acid or in fluorosulfonic acid. So, carbon-13 NMR has been found to be a very effective tool in the determination of the sequence distribution in a copolyamide chain. The carbonyl signal resonances of the copolyamides are sensitive for sequence distributions and can be analyzed in terms of diad sequences.[12] Another method is ^{15}N NMR, which makes it also possible to determine sequences; however, the advantage of proton and carbon NMR compared to ^{15}N NMR is that the quantitative measurements are more accurate.[7]

A few reports deal with the quantification of the copolyamide structure in terms of the number-average sequence (block) length and the degree of randomness. Kricheldorf et al.[12−14] have published results of copolymerizations for a binary copolyamide in terms of the average block length. More data were published for copolyesters,[17,18] whereas a complete theoretical description of the determination of the number-average block length and degree of randomness for a four-component polycondensate is given by Devaux et al.[19] Up to now, no detailed analysis of the structure of a four-component copolyamide, prepared in the molten state via transamidation reactions, has been published.

In this paper, the carbon NMR spectra of a blend and a copolymer of the semicrystalline aliphatic PA 46 and the amorphous aromatic PA 6I were studied. Both polyamide blend components are very suitable with respect to this study because of their miscibility over the whole composition range. The absence of multiple phases in the melt simplifies the investigation of transamidation reactions. Moreover, the chosen blend system has the added advantage of being of practical interest because both polyamide resins are commercially available products. The copolymer was formed after reaction in the molten state (melt-extrusion).[20]

On the basis of the NMR experiments, the diad sequence concentrations in the copolyamide are determined from the ^{13}C carbonyl resonance signals, and from these results the average copolymer composition, the number-average block length, the degree of trans-

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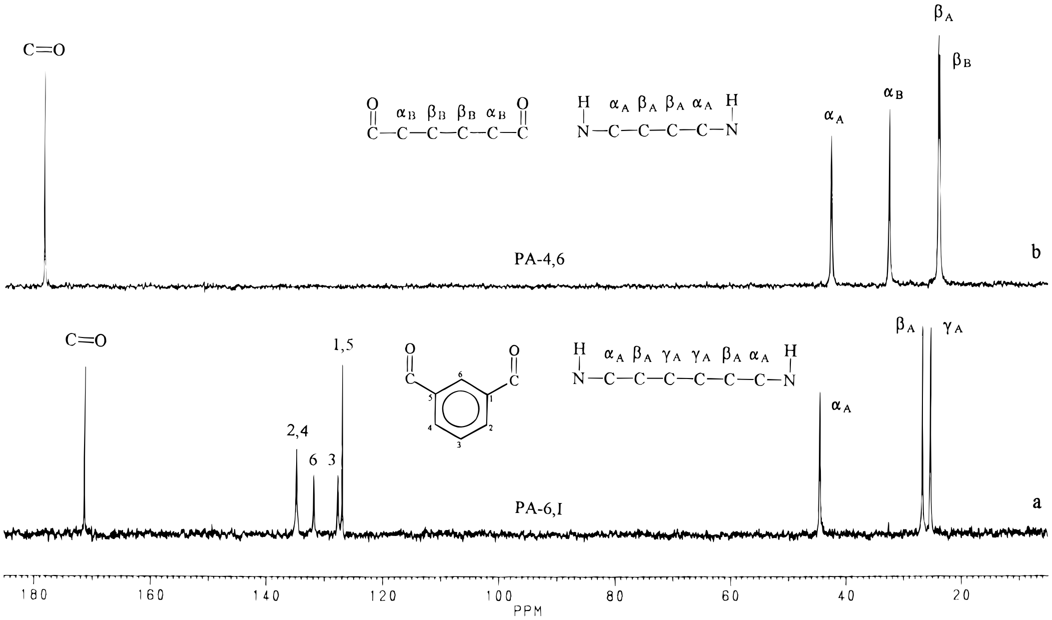


Figure 1. 62.5 MHz carbon-13 NMR spectra of (a) PA 6I and (b) PA 46 in D_2SO_4 at 60 °C.

amidation, and the degree of randomness could be computed.

Experimental Section

Materials. PA 46 (DSM, $M_n = 20\,700$) is a condensation product of 1,4-diaminobutane (DAB) and adipic acid (ADI). PA 6I (Bayer, $M_n = 8800$) is a condensation product of 1,6-diaminohexane (DAH) and isophthalic acid (IA).

Preparation of the Copolyamide. The preparation procedure of the copolyamide in the melt (melt-extrusion using a miniextruder) from the two homopolymers PA 46 and PA 6I is given in the accompanying paper.[20] In the present paper, a 50/50 composition is used. Melt-blending was performed at 315 °C during 90 min.

NMR Measurements. The ^{13}C NMR spectra were recorded at 62.5 MHz with a 250 MHz (Bruker) spectrometer at 60 °C. The sample concentration was 14% (w/v) in 98% sulfuric acid (D_2SO_4), as solvent and locking agent. The spectra were obtained after accumulating 10 000 scans with a digital resolution of 0.744 Hz/point, corresponding to a spectral width of 12 000 Hz and a data length of 16K. The flip angle and the pulse delay were 60° and 5 s, respectively.

In performing quantitative NMR measurements via compositional sequence and tacticity placements, one must take into account differences in spin−lattice relaxation times (T_1). No differential T_1's have been observed, and for the carbonyl signals, no differential NOE's were observed. The relative peak areas were measured by automatic integration methods.

Results and Discussion

Qualitative Interpretation of the NMR Spectra. From processes in the molten state of two homopolyamides, two questions have to be answered: first, do transamidation reactions take place so that a copolymer will be formed, and second, can we determine the number-average block length and the degree of randomness?

As mentioned before, carbon NMR is an effective tool to discriminate a blend and a copolymer.[9] Chemical shift differences in the carbonyl resonance signals of 1−3 ppm have already been observed by variation in the chain length.[12] More CH_2 groups in the monomeric unit of the nylons give rise to a shift to lower field of the carbonyl signal. Even the isomeric polyamide types can be discriminated in the carbonyl signal. The ^{13}C NMR spectra (Figure 1) of the homopolyamides PA 46 and PA 6I were measured to allow assignments of the signals of the copolyamides. The assignments of the carbon resonances of the homopolymers PA 46[21] and PA 6I are indicated in the figure.

According to the first question, to distinguish a blend of two homopolyamides of PA 46 and PA 6I (50/50) and a 50/50 copolymer of PA 46 and PA 6I, two carbon-13 NMR spectra (spectra b and a of Figure 2) were measured of a physical mixture of the two homopolyamides and of the reaction product of PA 46 and PA 6I obtained after 90 min of melt-mixing at 315 °C, respectively. Only the expansions of the carbonyl region are shown, since, in particular, this region shows additional splittings. In the expanded carbon NMR spectra of the carbonyl region, two new peaks (C and D) are clearly observed in the extruded reaction product (Figure 2a). From this spectrum, it can be concluded that transamidation reactions have taken place. The four signal peaks of the carbonyl carbon resonances can be explained in terms of diad sequence distributions (more spectra are shown in the accompanying paper[20]).

The exchange reaction taking place between PA 46 (composed of two monomeric units of different nature, ADI and DAB) and PA 6I (composed of IA and DAH) will give a four-component copolyamide. This can be represented by a general formula according to Devaux et al.:[19]

$$-[(A_1B_1)_x-(A_1B_2)_y]_m-[(A_2B_1)_z-(A_2B_2)_w]_n-$$

where A_1, A_2, B_1, and B_2 represent the monomeric units ADI, IA, DAB, and DAH, respectively. The letter indicates the monomer unit of different chemical nature (A is a dicarboxylic acid, B is a diamine) and the number indicates the original homopolymer. This means that A_1B_1 is the homologous sequence in PA 46 and A_2B_2 is the homologous sequence in PA 6I. Moreover, x, y, z, and w represent the average length of the various sequences; m and n are the mean lengths of blocks having in common the same A_1 or A_2 unit. The assignment of the four carbonyl carbon resonances in the copolyamide (Figure 2a) in terms of diad sequences is given in Table 1. The diad sequences can be measured quantitatively in the NMR spectra; the relative

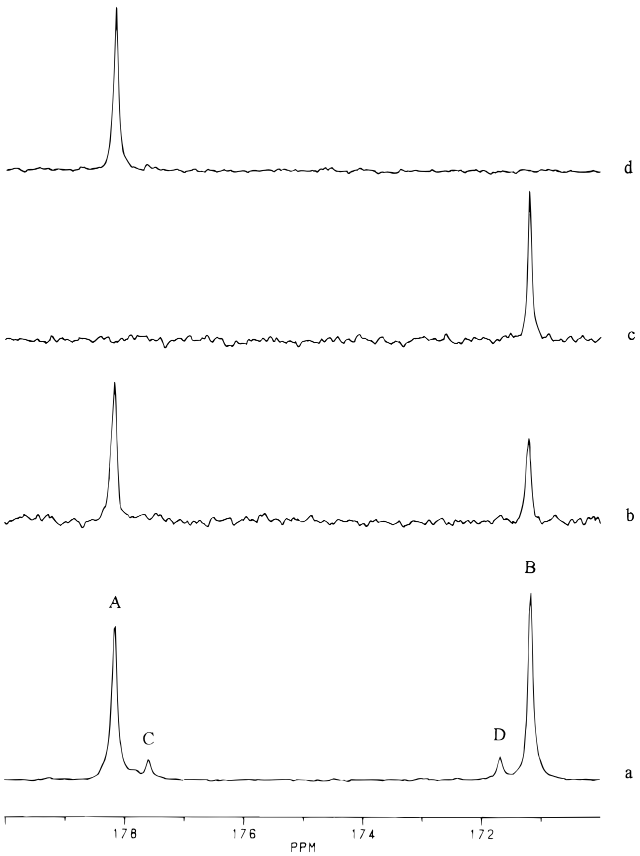
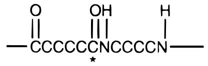
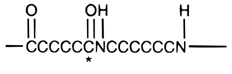
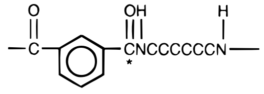
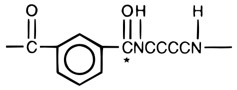


Figure 2. Expanded 62.5 MHz carbon-13 NMR spectra showing the carbonyl region only of (a) a reaction product after 90 min of extrusion at 315 °C of PA 46/PA 6I (50/50) in D_2SO_4 at 60 °C, (b) a 50/50 mixture of PA 46 and PA 6I, (c) PA 6I, and (d) PA 46.

Table 1. Assignment of the Carbonyl Resonances in the Copolymer PA 46/PA 6I

A 178.20 ppm	ADI−DAB (PA 46)	
C 177.62 ppm	ADI−DAH	
B 171.21 ppm	IA−DAH (PA 6I)	
D 171.71 ppm	IA−DAB	

peak areas of the diad sequences in the carbonyl signals are summarized in Table 2 and are compared with the theoretical values for a random copolymer of the same composition. At low degrees of transamidation the quantification of the different relative diad concentrations will be less accurate. The relative diad concentrations together with a statistical model made it possible to calculate the number-average lengths of the homologous blocks (next section) and the degree of randomness.

Percentage of Transamidation. The percentage of transamidation can be easily derived from the carbonyl region in the NMR spectrum of the reaction product after extrusion of two homopolyamides (Figure 2a). There will be 100% transamidation when all A_1B_1 units are changed into A_1B_2 units and all A_2B_2 units into A_2B_1 units. A completely random copolymer with a copolymer composition of 50/50 has 50% transamidation, having an equal amount of A_1B_1, A_1B_2, A_2B_2, and A_2B_1 units. Thus the percentage of transamidation (Ψ) can be calculated based on the fractions of A_1B_2 and A_2B_1 diad concentrations according the following formula:

$$\Psi\ (\%) = (F_{A_1B_2} + F_{A_2B_1}) \times 100\% \qquad (1)$$

where $F_{A_iB_j}$ is the fraction of an A_iB_j diad and is defined by

$$F_{A_iB_j} = \frac{[A_iB_j]}{\sum_{i=1}^{2}[A_i]} \qquad (i, j = 1, 2) \qquad (2)$$

The percentage of transamidation in the melt-mixed blend PA 46/PA 6I (50/50), whose NMR spectrum is shown in Figure 2a, is 12.16%. For other blend systems like PA 6/6,6 and PA 6/4,8, the degree of transamidation after 1 h at 295 °C is 20% and 45%, respectively.[12] There are various reasons why there are differences in the degree of transamidation between the different copolyamide systems.

In the accompanying paper,[20] the degree of transamidation and the degree of randomness as a function of the extrusion time, extrusion temperature, and polymer composition of the PA 46/PA 6I system is discussed.

Quantitative Determination of the Degree of Randomness and the Average Block Length. This section will give us the answer to the second question. Quantification of the degree of randomness and the number-average block length is defined by several groups for different systems. The analysis for a standard two-component AB copolymer is well explained by Koenig.[22] Other studies concern the structures of three-component polycondensates[17] and four-component polycondensates.[18,19] In our study, we have a four-component copolyamide system, and the same statistical model can be applied which was developed by Devaux et al.[19] for exchange reactions between two linear polycondensates $(A_1B_1)_p$ and $(A_2B_2)_q$ (p and q are the number of units in polymers 1 and 2, respectively) with degrees of polymerization high enough so that the effects of chain ends can be neglected in the calculations.

The following concentration relations are valid:

$$[A_i] = [B_i] \qquad (i = 1,2) \qquad (3)$$

$$[A_1B_2] = [A_2B_1] \qquad (4)$$

The degree of randomness is represented by

$$\chi = \frac{[A_iB_j]}{[A_1][A_2]} \qquad (i,j = 1,2) \qquad (5)$$

When a copolymer exhibits completely random statistics, then

$$[A_iB_j] = [A_1][A_2], \qquad \text{thus } \chi = 1 \qquad (6)$$

Values of $\chi > 1$ indicate that the units have a more alternating tendency. When $\chi < 1$, the units tend to cluster in homogeneous sequences and thus the copolymer exhibits a block character. When $\chi = 2$, then we have a completely alternating copolymer, and in the case when $\chi = 0$, the copolymer is completely block, or the system is a mixture of two polyamides.

Table 2. Experimentally Determined Diad Fractions of the Copolymer PA 46/PA 6I (50/50) Prepared in the Molten State at 315 °C for 90 min Compared with the Theoretical Values of a Physical Blend and a Random Copolymer with the Same Composition

	F_{A_1}	F_{A_2}	$F_{A_1B_1}$	$F_{A_1B_2}$	$F_{A_2B_2}$	$F_{A_2B_1}$
physical blend[a]	0.500	0.500	0.500		0.500	
random copolym[b]	0.500	0.500	0.250	0.250	0.250	0.250
extruded copolym[c]	0.484	0.516	0.423	0.060	0.455	0.061

[a] Physical mixture of the two homopolymers PA 46 and PA 6I. [b] Hypothetical random copolymer of PA 46/PA 6I. [c] Transamidated product of PA 46 and PA 6I after melt-mixing 90 min at 315 °C.

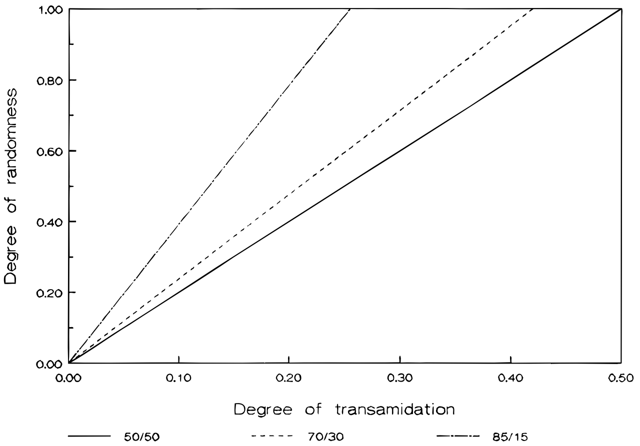


Figure 3. Degree of transamidation as a function of degree of randomness for (a) a 50/50 copolymer, (b) a 70/30 copolymer, and (c) an 85/15 copolymer of PA 46 and PA 6I.

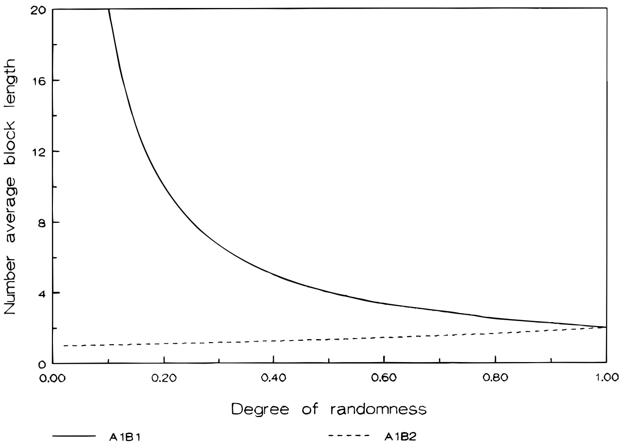


Figure 4. Number-average block length of A_1B_1 units (a) and A_1B_2 units (b) as a function of degree of randomness for a 50/50 copolymer.

In Figure 3, the general relation between the degree of randomness (χ) and the degree of transamidation (Ψ) is presented for a 50/50 copolymer and for the copolymers with the ratios 70/30 and 85/15.

$$\Psi = 2F_{A_1}F_{A_2}\chi \tag{7}$$

When the copolymer is completely random, then the percentage of transamidation for a 50/50 copolymer is 50%, and for the comparison of 70/30 and 85/15, the percentage of transamidation is 42% and 25.5%, respectively.

The number-average sequence length of A_1B_1 groups, x, is

$$x = \frac{1}{P_{A_1B_2}} = \frac{[A_1]}{[A_1][B_2]} = \frac{[A_1B_1]}{[A_1B_2]} + 1 \tag{8}$$

where $P_{A_iB_j}$ represents the probability of finding an A_i unit followed by a B_j unit ($P_{A_iB_j} = [A_iB_j]/[A_i]$).

In the same way the number-average lengths of the A_1B_2, A_2B_1, and A_2B_2 sequences, y, z, and w, respectively, are defined as

$$y = \frac{1}{P_{A_1B_1}} = \frac{[A_1]}{[A_1][B_1]} = \frac{[A_1B_2]}{[A_1B_1]} + 1 \tag{9}$$

$$z = \frac{1}{P_{A_2B_2}} = \frac{[A_2]}{[A_2][B_2]} = \frac{[A_2B_1]}{[A_2B_2]} + 1 \tag{10}$$

$$w = \frac{1}{P_{A_2B_1}} = \frac{[A_2]}{[A_2][B_1]} = \frac{[A_2B_2]}{[A_2B_1]} + 1 \tag{11}$$

In this particular case of the copolyamide system PA 46/PA 6I, there is the restricted ability of determining diad instead of triad sequences; so we have assumed from the theory of Devaux et al.[19] that in all triads the substitution on the left of a central unit does not influence the substitution on the right.

In a random copolymer with equal mole ratio of A_1 and A_2 (50/50), $\chi = 1$ and the number-average sequence length of A_1B_1 and A_2B_2 is x = 2 and w = 2. This can be observed in Figure 4, where the average block length of x and y is presented as a function of the degree of randomness. In the beginning of the transamidation reaction, there occurs a strong decrease in average block length till a randomness of 0.3, i.e., 15% transamidation. More transamidation corresponds to a further slow decrease in the average block length. In this particular example, the average number of A_1B_1 units is 104 at the beginning, and after 15% transamidation, the average number of A_1B_1 units next to each other is around 6.7. When the transamidation reaction is very quick in a polyamide system, it will be very hard to achieve long homologous block lengths. On the other hand, when the transamidation process is very slow, short block lengths (going to random structure) will be obtained after very long (mixing) times, and probably other reactions such as degradation will then be involved.

Furthermore, the mean lengths of blocks having in common the same A_1 or A_2 units, i.e., blocks of the aliphatic type or blocks of the aromatic type, i.e., m and n, respectively, can be determined and may provide some additional information. According to Devaux et al.,[19] it is deduced that

$$m = \frac{p}{(x + y)} \frac{F_{A_1}q}{(F_{A_1}q + F_{A_2}p)} \tag{12}$$

$$n = \frac{q}{(z + w)} \frac{F_{A_2}p}{(F_{A_1}q + F_{A_2}p)} \tag{13}$$

Table 3. Calculated Number-Average Sequence Lengths and the Degree of Randomness

	Ψ	x	y	z	w	m	n	χ
physical blend[a]	0.00	104.00			36.00			
random copolym[b]	50.00	2.00	2.00	2.00	2.00	17.10	28.14	1.00
extruded copolym[c]	12.16	8.01	1.14	1.13	8.44	7.18	12.04	0.24

[a] Physical mixture of the two homopolymers PA 46 and PA 6I. [b] Hypothetical random copolymer of PA 46/PA 6I. [c] Transamidated product of PA 46 and PA 6I after melt-mixing 90 min at 315 °C.

where p is the number of A_1B_1 units in polyamide 46 (polymer 1) and q is the number of A_2B_2 units in polyamide 6I (polymer 2). F_{A_1} and F_{A_2} are the mole fractions of polymer 1 and polymer 2 in the copolymer, respectively.

The results of the degree of randomness and number-average block length calculated from the diad sequences of the copolymer (see Figure 2a) are listed in Table 3. These data are compared with the theoretical values of an unreacted PA 46/PA 6I mixture and a statistical copolymer of the same composition. It is clear from the χ-value that the copolymer has a block character ($\chi < 1$). The value of x is approximately 8, which means that, on average, eight homologous groups consist of A_1B_1 units next to each other. From these results, it is obvious that the transamidation reactions in the melt do not readily provide a practical method for the preparation of a high molecular weight random copolyamide, even if this copolymer is prepared under extreme conditions of high temperature and long extrusion times. One or two percent transamidation will change the copolymer into the average sequence length of A_1B_1 units of 100 and 50, respectively; so this indicates that copolyamides with long block lengths are difficult to prepare.

The values of m and n are also given in Table 3 and compared with the theoretical values of a statistical copolymer of the same composition. In eqs 12 and 13, the thermal degradation of the copolyamide is not taken into account.

Conclusions

In the study of the reaction products of the extrusion of PA 46 and PA 6I by means of ^{13}C NMR, it is shown that exchange reactions have taken place. Four kinds of diad sequences could be determined in the carbonyl resonances in the ^{13}C NMR spectra of the copolyamides. A tentative assignment was made after comparing the ^{13}C NMR spectra of the two homopolyamides separately and the physical blend.

From the relative peak areas of the four different diad sequences in the copolyamides, it was possible to determine the number-average block length as well as the degree of randomness using the theory developed for polyesters.

It was shown that after extruding a 50/50 (w/w) blend of PA 46/PA 6I for 90 min at 315 °C, the degree of randomness was 24% and the average homologous block length of PA 46 was 8. The resulting copolymer can still crystallize as demonstrated in the accompanying paper.

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