Transamidation in Melt-Mixed Aliphatic and Aromatic Polyamides. 3. Molecular Characterization Using Gradient Elution Chromatography (GEC)

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ABSTRACT: Melt-mixing of blends of polyamide 46 (PA 46) and polyamide 6I (PA 6I) gives rise to the formation of copolymers on account of the occurrence of transamidation reactions. The degree of transamidation as obtained during the first minutes of melt-mixing is often too low to permit characterization by NMR or FTIR. To solve this problem, gradient elution chromatography (GEC) has been used. It is visualized using this technique to what extent transamidation is occurring during the first 10 min of melt-mixing. Also, the dependence of the reaction rate on the extrusion temperature has been studied using GEC. Melt-blending of PA 46 having varying end-group concentrations and end-group ratios with PA 6I does not seem to alter the elution behavior of the copolyamides formed; this indicates a transamidation mechanism of hydrolysis and recombination. Finally, it has been proved that degradation processes occurring during the residence time of the melt in the extruder do not influence the retention time of the polyamides in the column.

Introduction

Reactive extrusion has become a powerful tool in realizing a broad range of applications. Examples of using extruders as a chemical reactor are bulk polymerization,[1,2] controlled degradation,[3,4] polymer functionalization, and functional group modification.[5−8] Besides the previous applications, reactive compatibilization during melt extrusion has also become a well-studied topic because of the increasing importance of improving the blend properties by realizing a finer phase dispersion in an immiscible blend system. One of the methods to do so is in-situ formation of grafted[9−11] or cross-linked copolymers.[12,13]

Nonmiscible blends of polycondensates such as polyesters and polyamides can be compatibilized by creating linear block copolymers at the interface between the phases during meltextrusion. Meltextrusion of polycondensates will result in interchange reactions yielding diblock copolymers in the early stage of the extrusion process. During long extrusion times, the diblock copolymers are gradually being converted into segmented or even random copolymers composed of sequences of the initial blend components. This will in turn reduce the interfacial tension and enhance the phase dispersion and the interfacial adhesion.[14−18] In miscible polycondensate blends, transreactions will occur to a large extent because of the intimate contact between the components at a molecular level. If one succeeds in controlling the interchange reactions in these miscible blend systems during the melt-mixing process, it will be possible to design tailored block or random copolymers with potential useful properties. It has to be emphasized that increasing the degree of transreaction during melt-mixing of crystallizable and noncrystallizable polycondensates will result in a decrease of the crystallizable block lengths. This will reduce the crystallinity, which is often not desirable. Therefore, realizing a low degree of transreaction creating long segment block copolymers is more preferable.

Molecular characterization of block copolymers formed during reactive extrusion is often feasible using NMR or FTIR.[19−23] However, NMR and FTIR have their restrictions regarding the characterization of reactive blend systems with a low reaction rate. Because melt extrusion in most cases implies a short melt residence time, only a limited number of reactions will have occurred at the end of the extrusion process. The characterization of these reaction products by NMR or FTIR is becoming even more difficult if the chemical natures of the polymer bonds of the initial and the reacted products are very similar. This is the case if PA 46 and PA 6I are melt-mixed. The new amide bonds of the copolyamides which are formed as a result of transamidation reactions differ only slightly from the amide bonds of the homopolyamides. The only difference occurring during the transreaction processes is that some butane neighbors of the amide bonds are being replaced by a hexane neighbor and vice versa.

To overcome the resolution problem of NMR or FTIR with such blend systems, another method of characterization is needed. This technique is gradient elution chromatography (GEC). GEC is a high-performance liquid chromatography method which allows one to determine the chemical composition distribution (CCD) of copolymers.[24−29] A precipitation−redissolution mechanism combined with a distinct contribution of adsorption will make it possible to separate and characterize the copolymers. Polymers with a different chemical composition will have a precipitation−redissolution transition which occurs at different solvent compositions. The precipitation−redissolution mechanism hereby is obtained by using a two-solvent gradient, going from a nonsolvent A to a strong solvent B. Moreover, the adsorption/desorption transition of the chemically differing polymers will also occur at different solvent compositions when a polar column is being used. It is

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Table 1. Characteristics of PA 6I and PA 46 Batches

polyamide	M_n	M_w	M_z	amt of amine end group (mequiv/g)	amt of carboxyl end group (mequiv/g)
PA 46 *(batch 1)*	23 400	50 400	79 000	0.005	0.040
PA 46 *(batch 2)* (extruded pellets)	20 700	51 100	86 400	0.018	0.050
PA 46 *(batch 3)*	24 800	69 900	120 500	0.018	0.057
PA 6I (extruded pellets)	8 800	28 900	67 000	0.030	0.075

possible by this way to separate polymer blends into their components.

In this paper, GEC is used to characterize PA 46/PA 6I blends which have been melt-mixed during a short period (i.e. less than 10 min). The degree of transamidation after the melt-mixing process is lower than 5%. GEC appears to be a suitable characterization method for the study of the effect of the extrusion conditions (extrusion time and extrusion temperature) on the degree of transamidation. Also the possible influence of the molecular weight and the end-group concentration on the transamidation reaction rate has been examined. Melt-extrusion times of 15 min and longer yield a degree of conversion which is high enough to allow characterization by ^{13}C NMR.[30,31] This illustrates the complementary character of GEC and NMR/FTIR.

Experimental Section

Blend Components. PA 46 (obtained from DSM) is a condensation product of 1,4-diaminobutane and adipic acid. Several batches of PA 46 with varying end-group concentrations and different end-group ratios were used in this study (Table 1). PA 6I (product from Bayer) is a condensation product of 1,6-diaminohexane and isophthalic acid. The molecular characteristics are given in Table 1. All polyamides are commercial grade without additives.

Blend Preparation. All blends of PA 46 and PA 6I were first prepared via a dissolution–precipitation method; hexafluoroisopropanol has been used as a common solvent and deionized water, as a nonsolvent. The blend composition of PA 46/PA 6I was fixed at 90/10 (w/w). The obtained blends were first intensively dried at 100 °C for 48 h under vacuum and subsequently melt-blended using a minimixer. The blending time was varied between 0 and 10 min at 315 °C. One blend was been melt-mixed for 2 min at 300 °C. To approach a random copolymer, a blend composed of 30% PA 46 and 70% PA 6I was melt-mixed for 90 min at 315 °C.

GEC. The liquid chromatograph was a Model 1090 Type PV 5 (Hewlett-Packard, Waldbronn, FRG). The apparatus is equipped with an autosampler, autoinjector, and diode-array detector (DAD). The length and the internal diameter of the column are 100 and 2.1 mm, respectively. The column was packed with Hypersil, which is an octadecylsilica (pore diameter, $d_o \cong 10$ nm, particle diameter, $d_p \cong 5\ \mu$m). Hexafluoro-2-propanol was taken as the solvent, and water, as the nonsolvent. The gradient conditions were as follows: HFIP–H_2O with 0.1% TFA throughout, HFIP concentration = 55% at time zero and 82.5% at a time of 70 min. The flow rate was set at 0.2 mL/min. Detection by the DAD was done at 195–200 and 230–235 nm. The data were processed using a HP CHEMSTATION (MS-DOS series).

Results and Discussion

Preliminary GEC Runs. Transamidation will occur not only between chemically differing polyamides but also during melt-processing of each of the starting polyamides. This will result in a change of the molecular weight and molecular weight distribution toward an equilibrium.[32–34] The retention time of polymers in the GEC column can be dependent on the molecular weight of the polyamides or can be influenced by chemical reactions caused by degradation processes. To verify the impact of these factors on the retention time, some preliminary experiments have been performed.

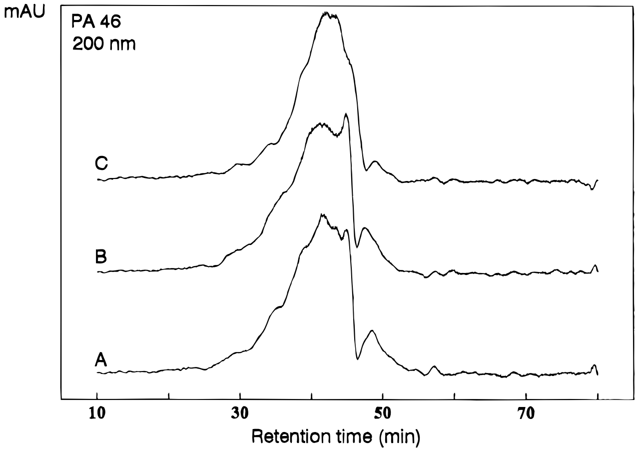

Figure 1. GEC chromatograms of PA 46 samples: (A) batch 1; (B) batch 2; (C) batch 3. Wavelength of detection: 200 nm.

Two batches of compacted powder of PA 46 with a different molecular weight were prepared to study the influence of the molecular weight of PA 46 on the retention time in the column. A third batch provides PA 46 with a similar molecular weight which has passed through the extruder one time. The molecular weights of the batches are given in Table 1. Figure 1 represents the GEC chromatograms taken at 200 nm for the different batches. It appears that the differences between these batches do not influence the retention time of PA 46. Even the extruded batch of PA 46 reveals an identical retention time.

It is known that melt-mixing of polyamides at high temperatures gives rise to thermal and oxidative degradation processes.[35,36] It is important to evaluate the effect of the degradation reactions on the retention time. This is done by sequentially melt-processing pure PA 46 and pure PA 6I during 10 min, which is the extrusion time range of the PA 46/PA 6I blending experiments which are performed. The resulting GEC chromatograms of the samples with different degradation levels taken at a detection wavelength of 200 nm are given in Figure 2 for PA 46. The retention time of the PA 46 appears to be independent of degradation processes occurring within the first 10 min of melt-mixing. There is also no visible effect of degradation processes on the retention time when looking at 235 nm where PA 6I can be detected; there is no shift in retention time nor peak broadening due to degradation processes.

Effect of Melt-Blending Conditions on the Degree of Transamidation. Influence of the Extrusion Time. Blends composed of 90 wt % PA 46 and 10 wt % PA 6I were first prepared by coprecipitation from a common solvent. It has been found in previous work that PA 46 and PA 6I are fully miscible, both by preparing blends from solution and by melt-mixing.[37] However, using the solution-prepared blends for the melt-mixing experiments excludes the melt-blending time which is needed to obtain a homogeneous melt. By following this procedure, the experimental extrusion

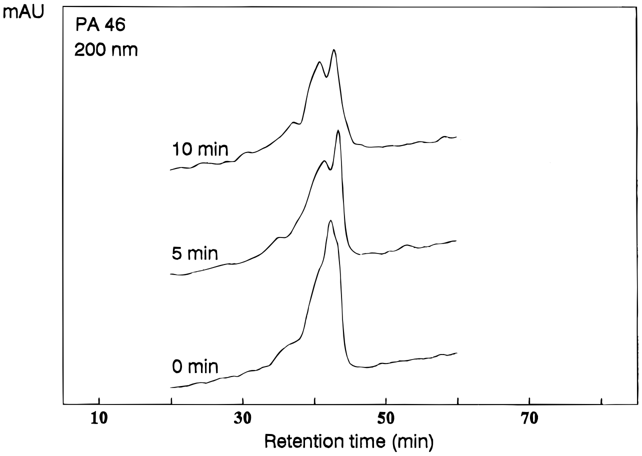

Figure 2. GEC chromatograms of the pure polyamide 46 as a function of the extrusion time. Wavelength of detection: 200 nm.

time is the actual reaction time without mixing effects. The reason for using a PA 46/PA 6I 90/10 ratio is the low reaction rate at this blend composition. The transamidation reactions can be better controlled by this way. Moreover, this blend composition yields an improved detection of the blend components leaving the column, because the aromatic PA 6I is highly absorbent at 230−235 nm (conjugated bonds) compared to the aliphatic PA 46 which is nonabsorbent at 235 nm and, as a consequence, is more difficult to detect. Therefore, it is useful to have a high concentration of PA 46 in the blend.

Figure 3 represents the GEC chromatograms of the blends taken at 195 nm as a function of the extrusion time. A GEC run has also been taken for a pure physical blend without transamidation reactions (t = 0). It can be seen that PA 46 and PA 6I can nicely be separated by a difference in retention time of about 30 min. When the blend is being melt-extruded, it can be noticed that the peak of PA 6I is systematically disappearing and a broad signal between the retention times of pure PA 46 and pure PA 6I is coming up. This broad signal can be ascribed to the formation of copolymers composed of PA 46 and PA 6I. The copolymers have a retention time which is intermediate between that of PA 46 and PA 6I. Figure 4 shows the same chromatograms but taken at 235 nm where only PA 6I can be detected. In this way, it is even more visible how homopolyamide 6I is being converted into copolymer during the melt-extrusion process. At first, the peak is broadening on the left hand side of the signal with increasing extrusion time but is simultaneously shifting to lower retention times as no pure PA 6I remains.

The GEC measurements can also be utilized to perform quantitative calculations of the transamidation processes as a function of the extrusion time. In order to do this, a third spectrum is needed which is the difference of the spectra recorded at 195 and 235 nm. The difference of the two spectra yields a chromatogram where only PA 46 is visualized. This is given in Figure 5. It is possible to correlate area and mass using standards of PA 46 and PA 6I. This is possible because the sensitivity of detection of both blend components does not alter when the homopolyamides are being transformed into copolymers. This has been experimentally verified. By using narrow time ranges for integration of the chromatograms (e.g. between 59 and 60 min of retention time) and using the correction factors of PA 46 and PA 6I obtained from the standards, one can calculate how much of the analyzed sample consists of a certain copolymer composition.

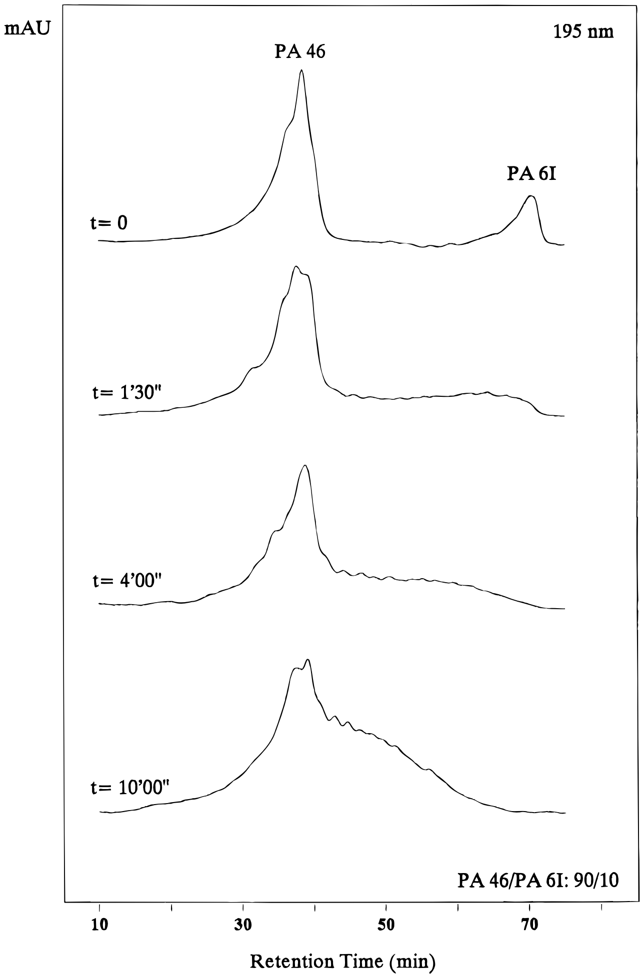

Figure 3. GEC chromatograms of PA 46/PA 6I (90/10 w/w) blends as a function of the extrusion time. Extrusion temperature: 315 °C. Wavelength of detection: 195 nm.

Figure 6 represents the mass distribution of PA 46 in the blend during the first 10 min of the melt-mixing process. It can be seen that in the beginning of the extrusion process (extrusion time = 0), all PA 46 exists in the form of homopolyamide (i.e., 90% of the blend). However, as the extrusion process proceeds, PA 6I is being added to PA 46 and copolymers are being formed. This can be seen by the decreasing mass of the homopolyamide 46 and the development of a broad shoulder next to the location of homopolyamide 46. This conversion process is even more visible in Figure 7 where the mass distribution of PA 6I in the blend is indicated. It has to be mentioned that the mass of pure PA 6I in the beginning of the extrusion process does not reach the 10% of the blend composition, as would be expected. This can be attributed to chromatographic peak broadening for which no correction was applied. The peak broadening is only significant at high PA 6I compositions due to the strong dependence of composition on the retention time with the used gradient (Figure 8). This effect could be minimized by applying a shallower gradient, but this in turn will increase the time needed for the experiment.

It can be seen from Figures 3 and 4 that the signals of the copolyamides are very broad, which indicates a large chemical composition distribution (CCD) of the

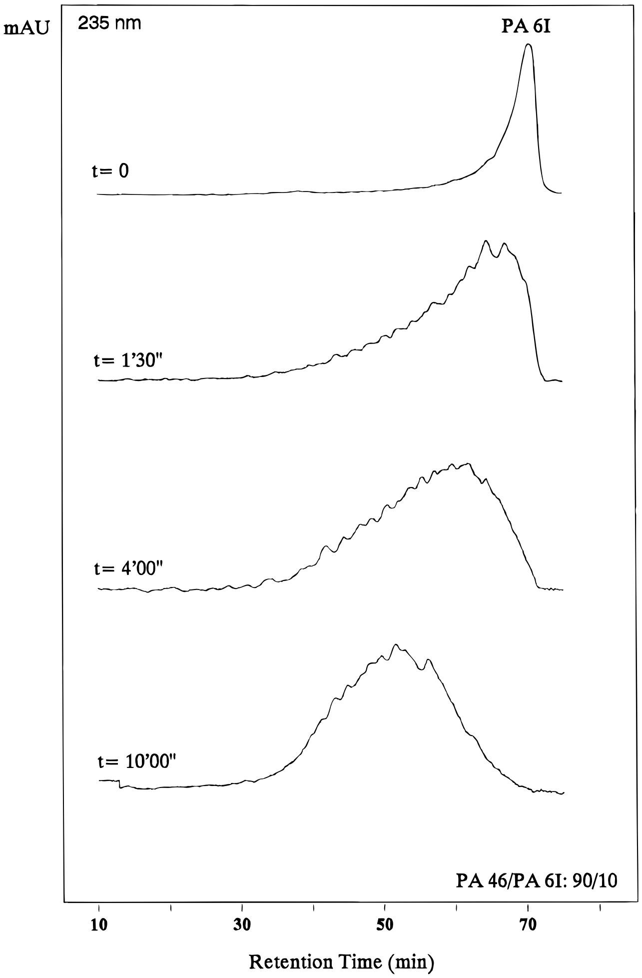

Figure 4. GEC chromatograms of PA 46/PA 6I (90/10 w/w) blends as a function of the extrusion time. Extrusion temperature: 315 °C. Wavelength of detection: 235 nm.

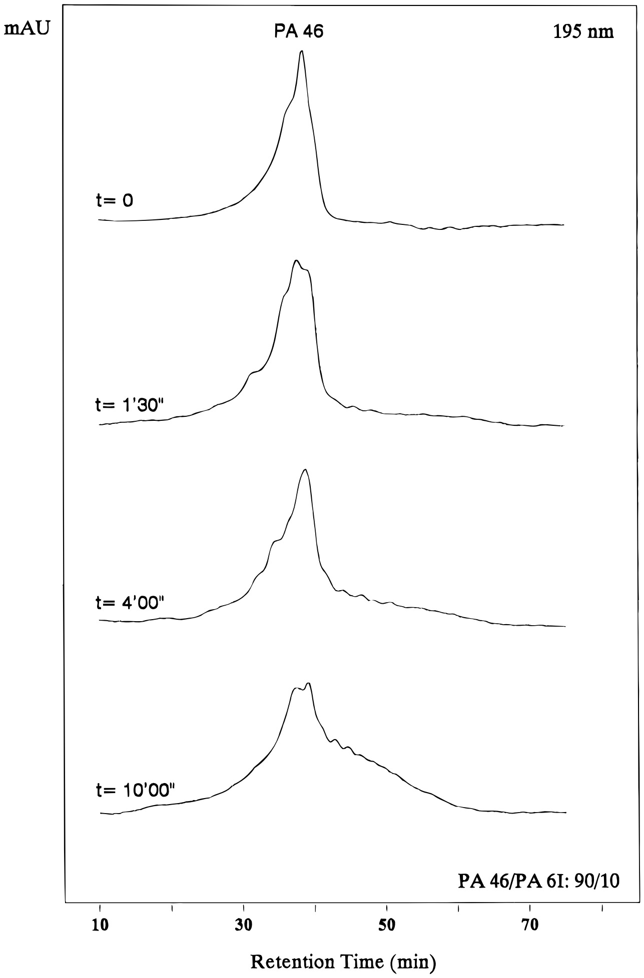

Figure 5. GEC chromatograms of PA 46/PA 6I (90/10 w/w) blends as a function of the extrusion time obtained by subtracting the chromatograms at 235 nm (PA 6I) from the chromatograms at 195 nm. Extrusion temperature: 315 °C.

copolymers. This implies that the copolymers formed during the first 10 min of melt-mixing are not random but block copolymers. A nearly random copolyamide will yield narrower signals such as illustrated in Figure 9. The nearly random copolymer is obtained by melt-mixing 30% PA 46 and 70% PA 6I during 90 min at 315°C.

Influence of the Extrusion Temperature. In a previous paper, the effect of the extrusion temperature on the transamidation reactions was described.[37] In order to study the increase of the reaction rate as a function of the extrusion temperature during short melt-mixing times, identical blend compositions were extruded during 2 min at different extrusion temperatures. One was extruded at 300 °C, while the second blend was extruded at 315 °C. The GEC chromatograms taken at 235 nm are given in Figure 10. A noticeable difference of the end products can be deduced from the chromatograms. It can be seen that the retention time of the copolymers obtained by melt-mixing at 315 °C is smaller than the retention time of the copolymers obtained by melt-mixing at 300 °C. The observed difference of the copolymers as a function of the extrusion temperature illustrates again the high sensitivity of GEC as a molecular characterization method.

Effect of End Groups on the Degree of Transamidation. In analogy with transesterification reactions, transamidation reactions can occur by different types of reaction mechanisms. Possible reaction types are reactions by the end groups (aminolysis and acidolysis) or direct interchange reactions (amidolysis). Studies of transesterification reactions in the past revealed that the dominant mechanism of transreaction in polyester blends composed of Bisphenol A polycarbonate (PC) and poly(butylene terephthalate) (PBT) or PBT and polyarylate (PAr) is direct transesterification.[38,39] However, the dominant reaction type in polyamide blends is still unknown.

One of the possibilities to verify whether the transamidation reactions are occurring via the end groups is to look for the occurrence of transamidation after making the end groups unavailable for transreaction processes using blocking groups. However, as mentioned above, melt-processing of polyamides causes degradation reactions during which new functional end-groups will be created. Another way to verify the influence of the end groups on the transamidation reactions is by varying the molecular weight and/or the ratio of amine/carboxyl end groups in one of the initial polyamides (i.e. before melt-blending) and then looking for differences in the resulting copolymers. Therefore, it is necessary to keep the extrusion time as short as possible because of possible degradation, causing new end-group ratios during melt-mixing.

In this series, the concentration of end groups and the end-group ratio of PA 46 has been varied. The PA 46 characteristics are given in Table 1. The melt-extrusion time was limited to 2 min. It has been

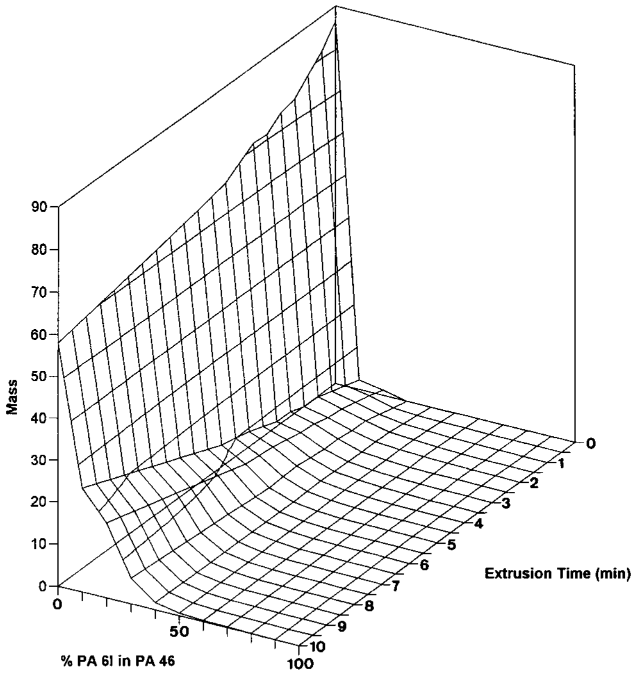

Figure 6. Mass distribution of PA 46 in the PA 46/PA 6I (90/10 w/w) blend as a function of the extrusion time. Extrusion temperature: 315°C.

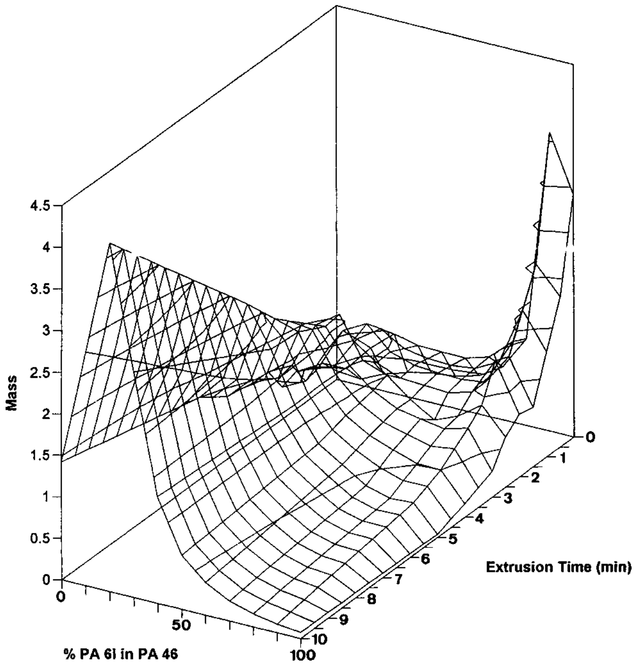

Figure 7. Mass distribution of PA 6I in the PA 46/PA 6I (10/90 w/w) blend as a function of the extrusion time. Extrusion temperature: 315°C.

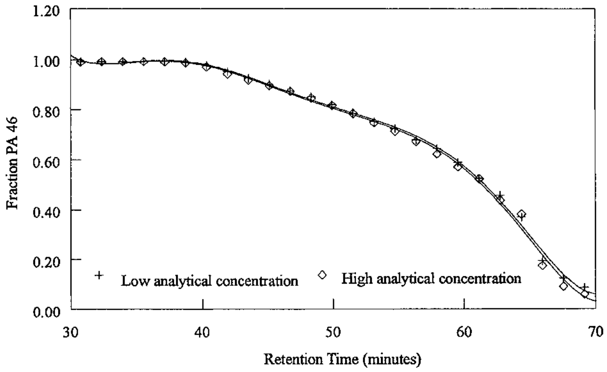

Figure 8. Calibration line of the fraction PA 46 in the PA46/PA 6I blend as a function of the retention time.

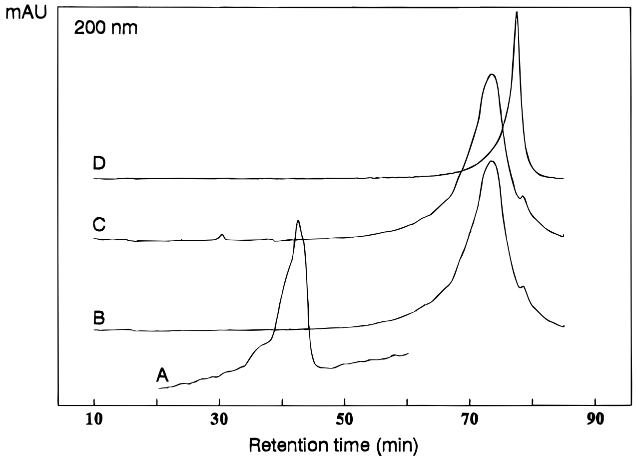

Figure 9. GEC chromatograms of pure extruded PA 46, pure extruded PA 6I, and nearly random PA 46/PA 6I copolyamides (30/70 w/w): (A) PA 46 (200 nm); (B) PA 46/PA 6I nearly random copolymers (200 nm); (C) PA 46/PA 6I nearly random copolymers (235 nm); (D) PA 6I (235 nm).

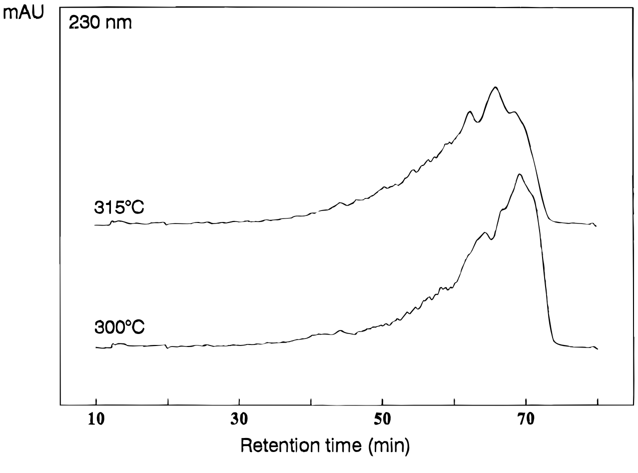

Figure 10. GEC chromatograms of PA 46/PA 6I (90/10 w/w) blends as a function of the extrusion temperature. Extrusion time: 2 min. Wavelength of detection: 235 nm.

observed that there is no significant influence of the end-group concentration of the initial PA 46 on the resulting chromatograms of the copolyamides after melt-mixing. The similarity of the elution behavior of the obtained copolyamides has also been noticed at 235 nm. There are no indications of a difference in reactivity depending on the end groups.

Because of previous observations, a transamidation mechanism is put forward which consists of hydrolysis followed by recombination (i.e. direct transamidation). Assuming this type of reaction, it is important to mention the influence of water and acid on the reaction rate. Moisture and acidity will catalyze hydrolysis of the polyamides which will accelerate the transamidation reactions. This has not been experimentally verified in this series of experiments, but these observations have already been done by Beste and Houtz in their work on transamidation reactions.[40]

Conclusions

Gradient elution chromatography appears to be a very suitable method for characterizing block copolymers of PA 46 and PA 6I resulting from transamidation reactions which occur during melt-mixing, even when the amount of transreaction processes is very limited. This is not feasible using NMR or FTIR because the concentration of new amide bounds in the copolymers under the given processing conditions is much too low to be detected. It has been verified that there is no influence of the molecular weight or degradation reactions on the retention time of the polyamides in the column. This implies that the observed changes in retention time are due to the formation of copolymers composed of the initial homopolyamides. The sensitivity of GEC is high enough to permit visualization of copolymer formation as a function of short extrusion times and varying extrusion temperatures. No indications have been found that there is any influence of the end-group concentration of the initial polyamides on the final block copolyamides. Therefore, it is assumed that transamidation is dominated by hydrolysis and recombination reactions.

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