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Structural Characterization of Copolyamides Synthesized via the Facile Blending of Polyamides

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ABSTRACT: Ny6-Ny6,10 and Ny6-Ny4,6 copolyamides prepared by a facile melt mixing at 290−310 °C of carboxyl terminated Nylon6 (Ny6-COOH) with Ny6,10 or Ny4,6, were characterized by MALDI, ^{13}C NMR, and DSC analysis. The results, from one side show how *facile* is the high yield synthesis of random copolyamides via the melt mixing of the corresponding polyamides. What makes the synthesis so *facile* is the use of a carboxyl terminated polyamide (Ny6-COOH) to attack the other polyamide (Ny4,6 or Ny6,10), as described herewith. The DSC data acquired provide a clear picture of the process. The second relevant point is about the sequence analysis of the copolyamides, made using their ^{13}C NMR spectra. The sequence has been derived directly from chain statistics principles, avoiding the use of inadequate procedures. To our knowledge, this is the first time as far as condensation copolymers are concerned. Interesting, the sequence analysis of our copolyamides has been also performed independently, by extracting pertinent information from their MALDI spectra. The results have been found in excellent agreement with those from ^{13}C NMR data.

Introduction

Widespread interest in the development of polymer blends with useful properties has resulted in numerous studies on the exchange reactions occurring in the melt mixing of polymer systems containing reactive functional groups.[1−10]

In the melt mixing process, variable amounts of random, block, and grafted copolymers are formed, which often act as partial compatibilizers of the initial blend, affecting the mechanical properties and the thermal stability of the resulting material.[10−14]

These exchange processes are important also from the synthetic point of view, since they make it possible to design tailored block or random copolymers with potentially useful properties. The synthesis of copolymers by means of reactive blending of homopolymers has now become a convenient route, which is an alternative to the usual copolymerization reactions that start from monomers.[1−7,15−17]

Exchange reactions may be induced by the presence of catalyst residues used in the polymerization, or may be caused by reactive terminal groups originally present in the polymers or generated in situ by thermal or hydrolytic degradation processes. Reactive functional groups, besides being located inside the polymer chains, may also be placed at the chain ends. Both inner and outer reactive groups may therefore be responsible for the chemical exchange reactions occurring in molten polymer blends.[1−27] Traditionally, workers have addressed the issue of reactive blending considering only the inner functional groups of the homopolymers repeat units, often forgetting about the role of reactive chain ends.[8−13,22]

In the past few years, we have approached this problem from a different point of view and have systematically investigated the exchange reactions occurring in the melt mixing processes of several condensation polymers, using both end-capped samples and polymers possessing reactive chain end groups.[1−7]

Our results indicate that several reactions proceed via the direct exchange between two functional groups located inside the polymer chains (referred to inner−inner exchange), and some other reactions occur via the attack of reactive chain ends on inner groups (referred to outer−inner exchange).[1−7]

According to our studies, ester exchange reactions (inner−inner processes) typically occur in polyesters and polycarbonates, whereas amide exchange reactions are not observed,[1−7] so that only acidolysis processes (outer−inner exchange) do occur in the melt mixing of polyamides.[4,14,18]

Failure to realize the importance of reactive chain ends has been a commonplace in many studies, and the role of end groups in the exchange process has remained somehow obscure. As a consequence, the overall picture of exchange reactions taking place in the reactive blending of materials as polyesters or polyamides, has often eluded the research efforts.[1−7]

Several workers have investigated various aspects related to the processing, compatibilization, morphology and mechanical properties of nylon blends.[14−22]

We report here a study on the reactive melt mixing process of two systems.

A low molar mass Ny6 terminated with carboxyl chain ends (Ny6-COOH) was melt mixed with high molar mass samples of Ny4,6 and of Ny6,10, respectively (Table 1). A combined MALDI and NMR analysis of the reaction products has allowed the identification

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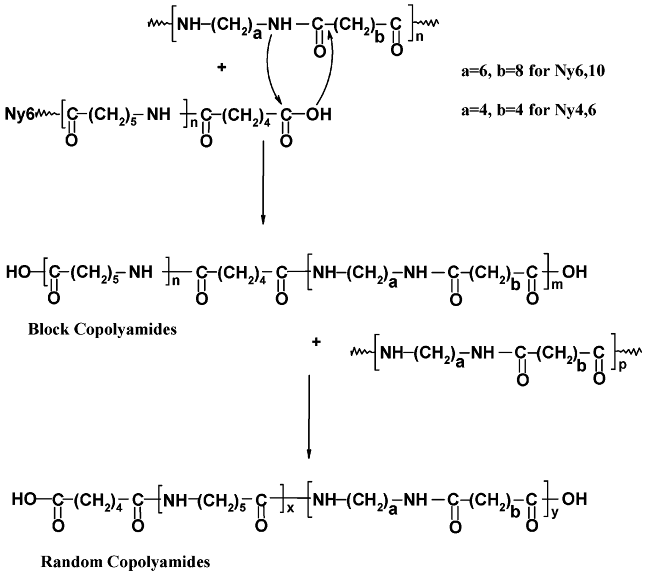
Table 1. Thermal Characteristics of Ny6, Ny6,10, and Ny4,6 Homopolymers and of the Equimolar Blends Ny6/Ny6,10 and Ny6/Ny4,6 Melt Mixed for Different Time and Temperature, As Derived from Their DSC Curves[a]

sample	homopolymers and blends	melt mixing conditions		T_g (°C)	T_c (°C)	ΔH_c (J/g)	T_m (°C)	ΔH_m (J/g)	% C[b]
		T (°C)	*t* (min)						
1	Ny6-COOH			59	158		206	82.9	44.3
2	Ny6,10			70			221	61.8	30.80
3	Ny4,6			78			292	80.8	35.0
4	Ny6-COOH/Ny6,10			64.	n.d.		206, 223	18.2, 40	34,[c] 28[c]
5	Ny6-COOH/Ny6,10	290	60	n.d.	60	9.2	198	50.6	25.7
6	Ny6-COOH/Ny6,10	290	120	n.d.	56	12.3	184	39.45	20
7	Ny6-COOH/Ny6,10	290	180	n.d.	55	15.1	172	43.11	21.9
8	Ny6-COOH/Ny6,10	310	10	n.d.	61	13.3	203	47.9	24.4
9	Ny6-COOH/Ny6,10	310	30	n.d.	60	16.2	188	44.11	22.4
10	Ny6-COOH/Ny6,10	310	60	n.d.	59.6	18.7	182	49	24.9
11	Ny6-COOH/Ny6,10	310	90	n.d.	60	18.2	182	48.2	24.6
12	Ny6-COOH/Ny4,6			69			209, 291	19.6, 39.5	28.8, 26.8
13	Ny6-COOH/Ny4,6	310	30	61			243[c]	63,66	29.6
14	Ny6-COOH/Ny4,6	310	60	59			243[c]	58, 94	27.4
15	Ny6-COOH/Ny4,6	310	90	60			243[c]	63.91	29.7
16	Ny6-COOH/Ny4,6	310	120	62			243[c]	58.64	27.2

[a] T_g = glass transition temperature; T_c = crystallization temperature, T_m = melting temperature; ΔH_c = normalized enthalpy of crystallization; ΔH_m = normalized enthalpy of melting. [b] The percentage of crystallinity of the homopolymers were calculated using specific heats of fusion for 100% crystalline Ny6 ($\Delta H°_m$ = 187.27 J/g), Ny6,10 ($\Delta H°_m$ = 205.75 J/g) and Ny4,6 ($\Delta H°m$ = 231.16 J/g) samples.[31] The crystallinity of all Ny6,10/Ny6-COOH blends are calculated for an average value (195.85 J/g) of the $\Delta H°_m$ of Ny6 and Ny6,10 samples, whereas those of Ny4,6/Ny6-COOH blends are calculated for an average value (215.22 J/g) of the $\Delta H°_m$ of Ny6 and Ny4,6 samples. [c] A small endothermic peak was also present at about 228 °C.

Scheme 1



of the structural details of the copolymers produced in the exchange.

The determination of the composition and the average block length of copolymers is usually performed by ^{13}C NMR methods, since the carbonyl signals are sensitive to chain sequences and can be analyzed in terms of dyads or higher sequences.[22−28] The same task can be also achieved using mass spectrometry (MS).[1−7] The problem of decoding the intensity of peaks appearing in the mass spectra of copolymers and of relating them to the comonomers sequence has been addressed,[29] providing a new method for deducing the sequence distributions and composition of comonomers in copolymers by MS techniques.[29−33]

The MS method has been successfully applied to the characterization of the copolymers obtained in the processing of several reactive blends.[1−7]

Experimental Section

Materials. Diphenylsulfone (DPSO) and all solvents used were purchased from Aldrich Chemical Co. (Italy). Deuterated solvents were supplied by Merck.

The MALDI matrix 2-(4-hydroxyphenylazo)benzoic acid (HABA) was analytical-grade material, purchased from Sigma Aldrich Chemical Co. (Italy) and used as supplied.

High molar mass (MM) Ny6, Ny6,10, Ny4,6 polymers used were analytical-grade products, purchased from Aldrich Chemical Co. (Italy) and used as supplied. These polymers were ground from pellets to fine powder by a grinder in the presence of solid CO_2, purified from the lower MM oligomers by appropriate solvent/no-solvent solution/precipitation method and then dried at 60 °C in a vacuum oven for 1 week, before being used. Some characteristics of these polymers are listed in Table 1, whereas their ^{13}C NMR resonance signals are reported in Table 4.

The average molar mass (M_v) of each polymer was determined by viscometry in *m*-cresol as solvent at 25°C: Ny6 (M_v = 34 100 g/mol), Ny6,10 (M_v = 36 100 g/mol), Ny4,6 (M_v = 30 500 g/mol). The above values were calculated applying the Mark−Houwink equation $[\eta] = KM_v^a$ and using published data for the coefficients *K* and *a*.[34]

Synthesis of Dicarboxyl Terminated Ny6. Nylon 6 containing carboxyl at both ends (Ny6-COOH) was obtained by partial acidolysis of purified commercial high molar mass nylon-6, with adipic acid, in a molar ratio 1/0.15, at 245 °C for 10 min, under nitrogen flow, in the presence of DPSO which reduce the melt viscosity.

Typically, 88.38 mmol of Ny6 and 15 g of DPSO were melted at 245 °C in a three angled neck round-bottom flask, by stirring under a stream of nitrogen. Then, 6.629 mmol of adipic acid were added, and the mixture was reacted for 10 min. After cooling, the mixture was washed several times with acetone at room temperature to remove the DPSO. The solid residue was dried at 60 °C under vacuum for 2 days. A M_v = 15 200 g/mol was determined by viscosimetric analysis in *m*-cresol at 25 °C.

Synthesis of Copolyamides by the Reactive Blending Process. The synthesis of Ny6-Ny6,10 and Ny6-Ny4,6 copolyamides was carried out by melt mixing of equimolar mixtures (with respect to the repeat units) either of Ny6-COOH/Ny610 (28.6/71.4 w/w) and Ny6-COOH/Ny4,6 (36.3/63.4 w/w) blends, at 310 °C for different times (see Table 1), according to Scheme 1. The Ny6-COOH/Ny6,10 blends were also reacted at 290°C for 60, 120, and 180 min (Table 1).

Typically, 2 g of equimolar mixtures of Ny6-COOH and Ny6,10 samples were placed in a glass reaction vessel and reacted under a stream of N_2, stirring at 310 °C, for different times (10−180 min). Each mixture, tacked at a fixed time, was quenched in a ice/salt bath and then analyzed by DSC, ^{13}C NMR, and MALDI-MS techniques.

Detection of Amino and Carboxylic End Groups. The concentration of amino and carboxylic terminal groups, in Ny6-COOH, Ny4,6, and Ny6,10 samples used in the present work, were determined by the procedure described in the literature.[3,4] Specific values (mequiv/kg) for the samples used in this study are as follows: for Ny6-COOH [NH_2] = n.d., [COOH] = 74.2; for Ny6,10 [NH_2] = 15, [COOH] = 42; for Ny4,6 [NH_2] = 13, [COOH] = 48.

NMR Spectroscopy. ^{13}C NMR spectra were obtained at 50 MHz with a Bruker A-CF 200 spectrometer at 35 °C, using deuterated 1,4-dioxane as locking agent in a microprobe NMR tube. Samples were dissolved in fluorosulfonic acid [40 mg/mL]. The spectra were recorded with the following acquisition parameters: sweep width, 10204 Hz; 65 536 data points, giving a digital resolution of 0,311 Hz per point and an acquisition time of 3.2 s. A pulse width of 4 ms and delay of 1 s were used for about 20 000 accumulations. The acquisition parameters were optimized in order to obtain for similar carbon types present similar relaxation rates, and therefore, reliable quantification of ^{13}C NMR is possible.

Selected ^{13}C NMR spectra were also recorded at 125 MHz, using a UNITY INOVA Varian NMR (500 MHz) spectrometer. No sensible advantage was however observed at this higher resolution.

MALDI−TOF Mass Spectrometry. The MALDI−TOF mass spectra were recorded in linear and reflectron modes, using a Voyager-DE STR instrument (Perseptive Biosystem) mass spectrometer, equipped with a nitrogen laser ($\lambda = 337$ nm, pulse width = 3 ns), working in a positive ion mode. The accelerating voltage was 25 kV, grid voltage and delay time (delayed extraction, time lag), were optimized for each sample to achieve the higher mass resolution (fwhm). Laser irradiance was maintained slightly above threshold.

Samples used for the MALDI analyses were prepared as follows. First, 10 μL of polymer solution (2−3 mg/mL in TFE) were mixed with 30 μL of HABA solution (0.1 M in TFE). This solution was added to 1−2 μL of cationization salt (KI 0.05 N), dissolved in a mixture of TFE/H_2O 1:1 v/v). Then 1 μL of each analyte/matrix/salt mixture was spotted on the MALDI sample holder and slowly dried to allow analyte/matrix cocrystallization.

The better MALDI mass spectra were obtained in reflectron mode.

MACO4 Calculation. MALDI−TOF MS data were analyzed by using the MACO4 program previously described.[4−7,29] MACO4 accepts as input the following: (a) the experimental mass spectrum, (b) the mathematical model that defines the distribution of comonomers along the chain and information about the type of process by which the oligomers subjected to MS were obtained, i.e., if they are preformed or obtained in a selective o nonselective cleavage process. The program generates the theoretical mass spectrum using the equation $I(A_mB_n) = f(PAA, PAB, PBA, PBB)$, where $I(A_mB_n)$ is the intensity of the mass peak corresponding to the A_mB_n oligomer, and P_{ij} describes the probability of finding component i after component j.

If a best fit is requested, the computer code varies the parameters associated with the selected mathematical model until it finds the best match between the observed and calculated data. MACO4 yields as output the parameters that give the best agreement and a listing of the corresponding to theoretical spectrum. The difference between observed and calculated values is expressed in terms of error by means of the Hamilton agreement factor[29] (AF): $AF = q\Sigma_i(I_i^{\exp} - I_i^{\text{calcd}})^2$; where $I_i^{\exp}$ and I_i^{calcd} are the normalized experimental and calculated abundances of the oligomers and where the normalized factor q is given by $q = 1/(\Sigma_i(I_i^{\exp})^2)^{0.5}$

By means of this program the sequence distributions, composition, average sequence length, the degree of randomness and extent of exchange of the Ny6/NY6,10 and Ny6/Ny4,6 copolyamides prepared by melt mixing of the corresponding homopolyamides can be obtained.

DSC Measurements. The thermal properties (T_g, T_m, and T_c) of all samples in Table 1 were determined by an indium calibrated Mettler DSC 20 instrument, in a dry N_2 atmosphere, using a heating rate of 10 °C/min, from 25 to 310 °C. The T_g values were computed by the midpoint method; the melting point temperatures (T_m) were taken as the maximum of the endothermic peak, and the crystallization temperatures T_c were taken as the maximum of the exothermic peak. Values reported in Table 1 represent the average of several runs ($\Delta T = \pm 1$ °C).

NMR Calculations. The composition, the sequence distributions, the average sequence length, and the degree of randomness of the Ny6/NY6,10 and Ny6/Ny4,6 copolyamides synthesized were calculated from the intensities of carbonyl peaks in the ^{13}C NMR spectra, using a appropriate statistical model that we have developed (eqs 1−8).

This statistical model takes into account (see Discussion section) that diacid moiety in the Ny6,10 and in the Ny4,6 units, have two carbonyls, whereas only one is present in the Ny6 units.

$$2(I_{AA} + I_{AB}) = C_A/C_B(I_{BB} + I_{BA}) \qquad (1)$$

$$F_{AA} = C_A I_{AA}/(I_{AA} + I_{AB}) \qquad (2)$$

$$F_{AB} = C_A I_{AB}/(I_{AA} + I_{AB}) \qquad (3)$$

$$F_{BA} = C_B 2I_{BA}/(I_{BB} + I_{BA}) \qquad (4)$$

$$F_{BB} = C_B(I_{BB} - I_{BA})/(I_{BB} + I_{BA}) \qquad (5)$$

$$\langle A-A \rangle = 1/F_{AB}C_A \qquad (6)$$

$$\langle B-B \rangle = 1/F_{BA}C_B \qquad (7)$$

$$B = F_{AB}/C_A + F_{BB}/C_B \qquad (8)$$

In these equations, C_A and C_B indicate the molar concentration of component A (Ny6) and of component B (Ny6,10 or Ny4,6), respectively, in the copolyamides; F_{AA}, F_{AB}, F_{BA}, and F_{BB}, indicate the molar fractions of the AA, AB. BA and BB dyads, respectively; I_{AA}, I_{AB}, I_{BA}, and I_{BB} indicate the intensity of their corresponding carbonyl peaks in the ^{13}C NMR spectra; B indicates the degree of randomness; $\langle A-A \rangle$ and $\langle B-B \rangle$ indicate the average sequence length.

Equation 1 permits the calculation of the molar composition of A and B copolymer components from the intensity of the carbonyl signals.

Results and Discussion

In a previous study,[4] we have shown that the exchange reaction occurring during the melt mixing of Ny6,6 and Ny6,10 polyamides involves specifically the attack of carboxyl chain ends to the amide inner groups.

Furthering our studies, in the present work we have synthesized several Ny6/Ny6,10 and Ny6/Ny4,6 copolyamides, by the facile melt mixing of equimolar mixtures of Ny6-COOH with Ny6,10 and with Ny4,6, respectively, (Scheme 1).

The DSC data corresponding to the 16 polymer samples investigated are reported in Table 1. The first three columns report the type of polymer, the time and the temperature of processing. Three samples are homopolymers, two are physical mixtures, whereas 11 samples are equimolar blends melt mixed at 290 or 310 °C. Columns 4−9 report the glass transition (T_g), the crystallization temperature (T_c), the melting point (T_m), ΔH_c, ΔH_m and the degree of crystallinity. Ny6-COOH shows a T_g of 59 °C and a T_m of 206 °C ($\Delta H_m = 82.9$ J/g), whereas for Ny6,10, the T_g is 70 °C and T_m 221 °C

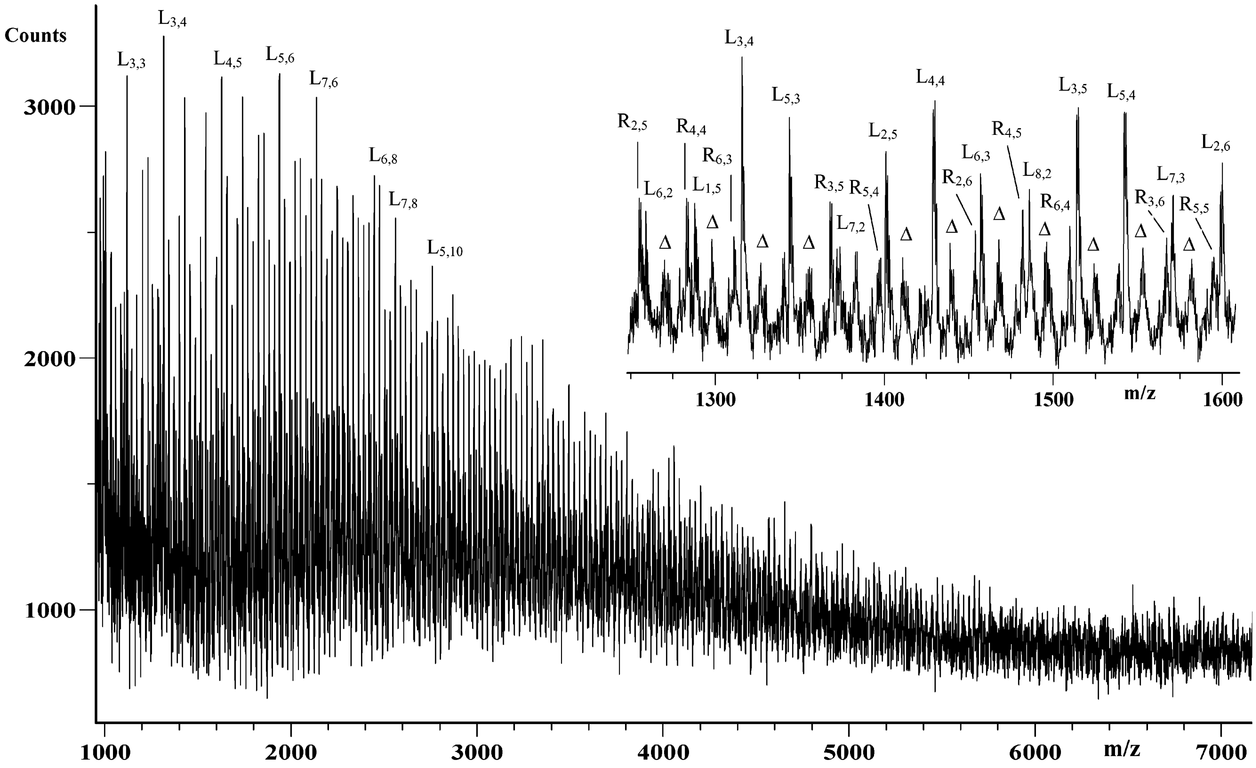


Figure 1. MALDI spectrum of the Ny6/Ny4,6 blend melt mixed at 310 °C for 30 min. Peaks labeled $L_{x,y}$ and $R_{x,y}$ indicate linear and cyclic co-oligomers, respectively, containing *x*Ny6 units and *y*Ny4,6 units. The inset shows the spectrum in the mass range 1190−1620 Da.

($\Delta H_m = 61.8$ J/g), and for Ny4,6, the T_g is 78 °C and T_m 292 °C ($\Delta H_m = 80.8$ J/g). The three homopolymers show a degree of crystallinity in the range of 44−31%, whereas for the melt mixed blends this varies in the range 22−30%. The degrees of crystallinity were calculated using the specific heat of fusion for the 100% crystalline polymer samples reported in Table 1.

The inspection of Table 1 reveals that each physical blend (Ny6/Ny4,6 and Ny6/Ny6,10), presents two T_m , whereas the melt mixed materials show a single T_m. The T_m of both blends decreases with the reaction time, reaching a final value of 182 °C for the Ny6/Ny6,10 blend and of 243 °C for the Ny6/Ny4,6 blend. This indicates that some reaction is occurring in these systems.

Another interesting feature in Table 1 is that both physical blends (Ny6/Ny4,6 and Ny6/Ny6,10) show a single T_g, at 69 and 64 °C respectively (Table 1), indicating that probably the polyamides yield compatible blends.[11,12] Therefore, one can expect the exchange kinetics in these systems be faster with respect to systems that form incompatible blends.

The T_g is no more observed for the melt mixed Ny6/Ny6,10 blends, which show an exothermic peak at about 60 °C (T_C, Table 1) due to a cold-crystallization phenomenon.[21]

The DSC data, although suggesting that the melt mixing process has produced copolymers, constitute only a phenomenological evidence. Therefore, to proceed to the structural characterization of the copolyamides produced we have performed a combined MALDI-MS and ^{13}C NMR analysis.

In Figure 1 is shown the MALDI spectrum of the Ny6-COOH/Ny4,6 blend melt mixed at 310 °C for 30 min. All the peaks in Figure 1 are due to AB co-oligomers that desorb and ionize as pothassiated adduct (Table 2), since the KI was added as cationizing agent the matrix/analyte mixture. Peaks labeled $L_{x,y}$ indicate linear oligomers containing *x*Ny6 and *y*Ny4,6 units, whereas peaks labeled $R_{x,y}$ indicate cyclic oligomers. The inset in Figure 1 shows an expanded portion of the spectrum in the mass range 1190−1620 Da. Detailed peak assignments are given in Table 2.

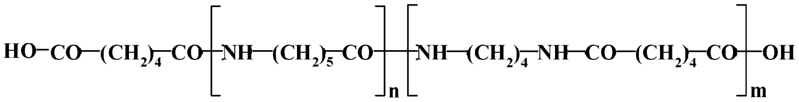
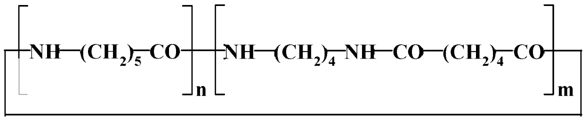
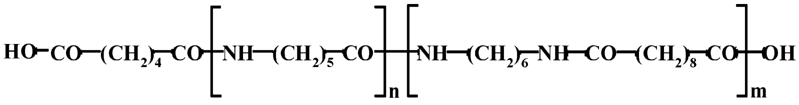
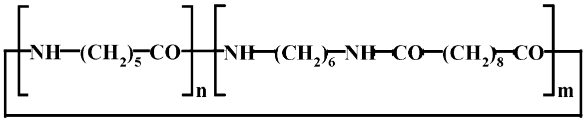
The kinetics of exchange reaction in the Ny6-COOH/Ny4,6 melt mixed blends can be followed by monitoring changes in peak intensity as a function of melt mixing time, and Figure 1S reports the MALDI spectra of the blends melt mixed at 310 °C for 30, 60, 90 min. It can be seen that the relative intensity of the peaks corresponding to blocky sequences such as $L_{1,5}$ and $L_{2,5}$ decreases, whereas the intensity of nearly equimolar peaks such as $L_{3,4}$ and $L_{4,3}$ increases with the melting mixing time, indicating that the exchange reaction proceeds toward the formation of a random copolyamide.

In Figure 2 is shown the MALDI spectrum of the Ny6-COOH/Ny6,10 blend melt mixed at 310 °C for 30 min. Peaks labeled $L'_{x,y}$ indicate the linear oligomers containing *x* Ny6 and y Ny6,10 units, whereas peaks labeled $R'_{x,y}$ indicate the cyclic oligomers. The inset in Figure 2 shows an expanded portion of the spectrum in the mass range 1190−1850 Da, and in Table 2 are reported the structural assignments.

The kinetics of exchange reaction was followed by monitoring changes in peak intensity as a function of the temperature and melt mixing time, and a behavior similar to the Ny6-COOH/Ny4,6 blend was observed.

In Figures 1 and 2, each species $L_{x,y}$ and $L'_{x,y}$ is accompanied at a mass lower than 18 Da by a peak marked with a symbol Δ, corresponding to the linear oligomers terminated at one end with carboxylic groups and at the other end with cyclopentanone moiety

Table 2. Assignments of the Peaks Present in the MALDI Spectra of the Ny6-COOH/Ny46 and of the Ny6-COOH/Ny6,10 Melt-Mixed Blends, Reported in Figures 1 and 2, Respectively

Species	Structure	n,m	$(M+K)^+$
L	 $HO-CO-(CH_2)_4-CO-[NH-(CH_2)_5-CO]_n-[NH-(CH_2)_4-NH-CO-(CH_2)_4-CO]_m-OH$	6,2	1260.5
		1,5	1289.3
		3,4	1317.4
		5,3	1345.5
		2,5	1402.5
		4,4	1430.6
		6,3	1458.7
		8,2	1486.8
		3,5	1515.6
		5,4	1543.7
		7,3	1571.8
		2,6	1600.7
R	 $[NH-(CH_2)_5-CO]_n-[NH-(CH_2)_4-NH-CO-(CH_2)_4-CO]_m$	2,5	1256.3
		4,4	1284.4
		6,3	1312.5
		8,2	1340.6
		3,5	1369.4
		5,4	1397.5
		7,3	1425.6
		2,6	1454.5
		4,5	1482.6
		6,4	1510.7
		8,3	1538.8
		3,6	1567.6
		5,5	1595.7
L’	 $HO-CO-(CH_2)_4-CO-[NH-(CH_2)_5-CO]_n-[NH-(CH_2)_6-NH-CO-(CH_2)_8-CO]_m-OH$	4,2	1202.6
		2,3	1258.8
		5,2	1315.8
		3,3	1371.7
		1,4	1428.1
		6,2	1429.1
		4,3	1485.1
		2,4	1541.0
		5,3	1598.3
		3,4	1654.7
		6.3	1711.5
		4,4	1767.6
		2,5	1824.0
R’	 $[NH-(CH_2)_5-CO]_n-[NH-(CH_2)_6-NH-CO-(CH_2)_8-CO]_m$	3,3	1225.8
		6,2	1282.8
		4,3	1338.9
		2,4	1395.0
		5,3	1452.1
		3,4	1508.2
		6,3	1565.2
		4,4	1621.3
		7,3	1678.3
		5,4	1734.5
		3,5	1790.7

generated by thermal decomposition reaction of the adipic acid terminal units.[35]

In the MALDI spectra in Figures 1 and 2 are present only peaks corresponding to co-oligomers, whereas are absent peaks corresponding to the hompolyamides. This indicates that the exchange reaction is fast at 310 °C and that even at the lowest melt mixing time explored (10 min, Table 2) the reaction went to completion.

The composition and the sequential arrangement of comonomer units present in the copolymers can be deduced from the mass spectra.[29−33] The MACO4 program[29−31] was employed to simulate the experimental data and to characterize the sequence distribution in Ny6/Ny4,6 and in Ny6/Ny6,10 copolyamides, using the normalized intensity of the peaks corresponding to the co-oligomers in the MALDI spectra of each sample, and the results are reported in Table 3. It can be noticed that all the copolyamides have a composition close to that of initial blend, i.e., equimolar, as expected for an exchange process carried out to completion.[1−7] The extent of exchange and the degree of randomness (B) are very high (Table 3), indicating a high rate of exchange and the formation of random copolyamides, due to the presence of a high concentration of reactive carboxyl chain ends.

At the beginning of the exchange process the carboxyl end groups of Ny6 attack the inner amide groups of Ny4,6 and Ny6,10 homopolymers; thus block copolyamide chains should be generated in the first steps of the reaction (Scheme 1). On the contrary, the MALDI data show that the copolyamides have a random distribution of sequences, suggesting that they are formed

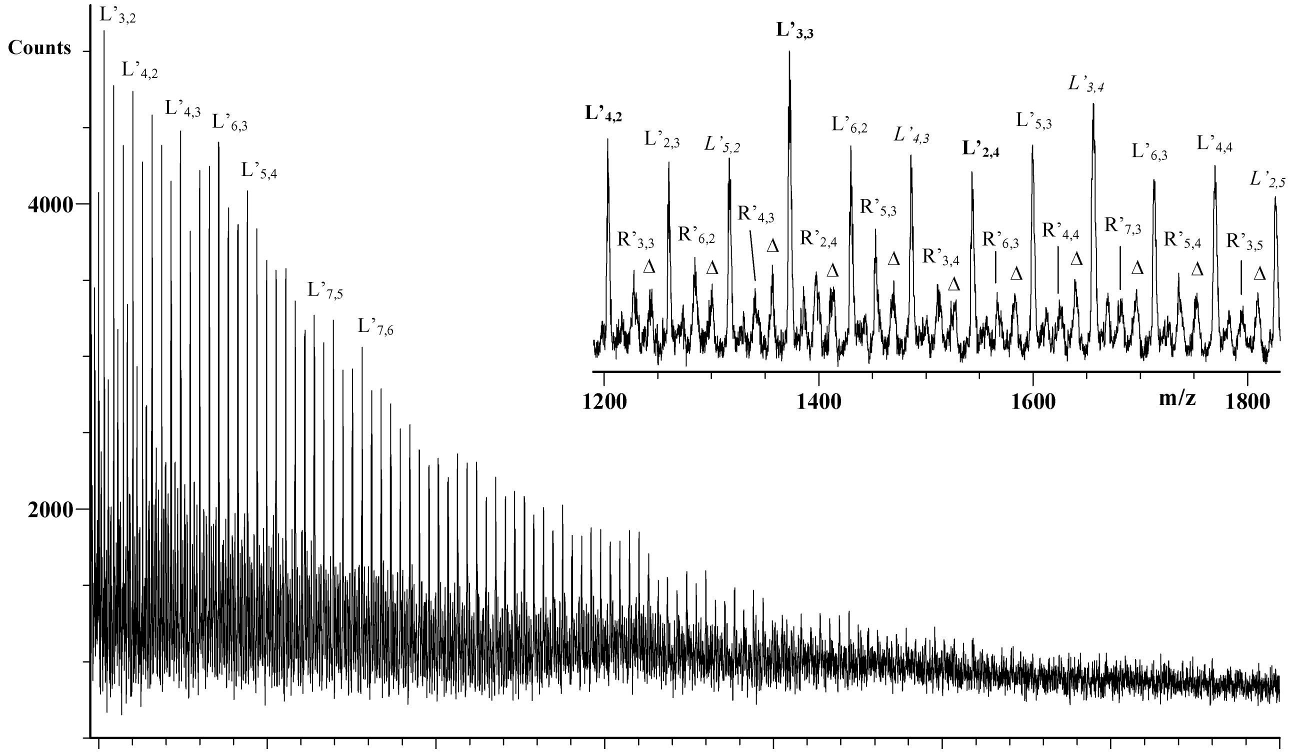


Figure 2. MALDI spectrum of the Ny6/Ny6,10 blend melt mixed at 310 °C for 30 min. The inset reports a portions of the spectrum in the mass range 1190−1850 Da. Peaks labeled $L'_{x,y}$ and $R'_{x,y}$ indicate cyclic and linear co-oligomers, respectiely, containing *x*Ny6 units and *y*Ny6,10 units. The examers and the eptamers are marked with bold and italic characters, respectively.

Table 3. Copolymer Compositions, P Matrix Elements, Average Sequence Lengths, and Degree of Randomness (*B*) of the Copolyamides Formed during the Melt Mixing of Equimolar Ny6/Ny6,10 and Ny6/Ny46 Blends, Calculated from MALDI Mass Spectra Using the MACO4 Program[a]

temp (°C)	time (min)	copolymer composition C_A/C_B	**P** matrix elements				molar fraction of dimers[b]				average sequence lengths		
			P_{A-A}	P_{A-B}	P_{B-A}	P_{B-B}	F_{A-A}	F_{A-A}	F_{B-A}	F_{B-B}	A−A	B−B	B[c]
Ny6-COOH/Ny6,10													
290	120	51/49	0.69	0.30	0.32	0.68	0.35	0.16	0.16	0.33	3.3	3.2	0.62
290	180	50/50	0.59	0.41	0.42	0.58	0.30	0.21	0.21	0.29	2.5	2.4	0.83
310	10	52/48	0.63	0.34	0.35	0.59	0.35	0.17	0.18	0.30	2.7	2.5	0.68
310	30	51/49	0.58	0.42	0.43	0.57	0.30	0.21	0.21	0.28	2.4	2.3	0.85
310	60	51/49	0.53	0.47	0.50	0.50	0.26	0.25	0.25	0.24	2.2	2.0	0.97
Ny6-COOH/Ny4,6													
310	30	48/52	0.57	0.43	0.40	0.60	0.27	0.21	0.21	0.31	2.30	2.60	0.83
310	60	47/53	0.49	0.51	0.44	0.56	0.23	0.24	0.23	0.30	1.98	2.23	0.95
310	90	47/53	0.47	0.53	0.49	0.51	0.22	0.25	0.26	0.27	1.98	2.06	1.02
310	120	47/53	0.43	0.57	0.53	0.48	0.20	0.27	0.27	0.26	1.75	2.10	1.05

[a] A indicates the Ny6 units whereas B indicates the Ny4,6 or Ny6,10 units in the copolyamides. [b] $F_{A-A} = P_{A-A}C_A$; $F_{A-B} = P_{A-B}C_A$; $F_{B-A} = P_{B-A}C_B$; $F_{B-B} = P_{B-B}C_B$. [c] $B = P_{A-B} + P_{B-A}$.

through an exchange process involving a fast acidolysis reaction.

The structural characterization of the Ny6-Ny6,10 and Ny6-Ny4,6 copolyamides synthesized was also performed by ^{13}C NMR.

The carbonyl resonance signals of the copolyamides are sensitive to changes in the sequence length distributions and, when the polyamides are dissolved in sulfuric acid or fluorosulfonic acid, chemical shift differences are observed in the ^{13}C carbonyl region for blends of polyamides, and alternating or random copolyamides.[23−27]

The assignments of the chemical shift of the carbonyls, and of the methylenes linked to the amide groups are reported in Table 4. Portions of the ^{13}C NMR spectra are reported in Figures 3 and 4.

Figure 3 reports relevant ^{13}C NMR peaks for the Ny6-COOH/Ny6,10 blends melt mixed at 310 °C for 0, 10, 30, and 60 min, whereas Figure 4 reports those of the Ny6-COOH/Ny4,6 blends melt mixed at 310 °C for 0, 30, 60, and 120 min.

Two new carbonyl peaks, in the range 178−180 ppm, are clearly observed in the carbon spectra of melt mixed blends (Figures 3 and 4). A similar behavior is observed in the region between 43 and 44 ppm where resonate the methylene carbons linked with the nitrogen of the amide groups (Table 4). The relative intensity and the number of signals due to the methylene linked with the carbonyl of the amide groups, which resonate in the region between 33 and 34 ppm (Figures 3 and 4, Table 4), does not change as the reaction time increases and their relative intensity reflects the molar compositions of the comonomers A (Ny6) and B (Ny6,10 or Ny4,6) in the copolyamides.

From Figures 3 and 4, is evident that the two systems present the same behavior, and we shall discuss only

Table 4. Assignments of the Dyads Present in the Copolyamides Formed during Melt-Mixing of Ny6-COOH/Ny6,10 and Ny6-COOH/Ny4,6 Blends, As Observed in their ^{13}C NMR Spectra (See Figures 3 and 4)

Dyads[a]	Structure	Carbon	Chemical Shift (ppm)
A-A (Ny6-Ny6)	$-NH-\overset{\alpha}{CH_2}-(CH_2)_3-\overset{\varepsilon}{CH_2}-\overset{\mathbf{a}}{CO}-NH-\overset{\alpha}{CH_2}-(CH_2)_3-\overset{\varepsilon}{CH_2}-CO-$	a α ε	179.27 43.65 33.65
B-B (Ny6,10-Ny6,10)	$-NH-(CH_2)_5-\overset{\delta}{CH_2}-NH-\overset{\mathbf{d}}{CO}-\overset{\phi}{CH_2}-(CH_2)_6-\overset{\phi}{CH_2}-\overset{\mathbf{d}}{CO}-NH-\overset{\delta}{CH_2}-(CH_2)_4-\overset{\delta}{CH_2}-NH-\overset{\mathbf{d}}{CO}-\overset{\phi}{CH_2}-(CH_2)_6-\overset{\phi}{CH_2}-CO-$	d δ ϕ	179.56 43.91 33.88
A-B (Ny6-Ny6,10)	$-NH-(CH_2)_4-\overset{\varepsilon}{CH_2}-\overset{\mathbf{b}}{CO}-NH-\overset{\gamma}{CH_2}-(CH_2)_4-\overset{\delta}{CH_2}-NH-\overset{\mathbf{d}}{CO}-\overset{\phi}{CH_2}-(CH_2)_7-CO-$	B d γ ε δ	178.96 179.56 44.01 33.65 43.91
B-A (Ny6,10-Ny6)	$-NH-(CH_2)_5-\overset{\delta}{CH_2}-NH-\overset{\mathbf{d}}{CO}-\overset{\phi}{CH_2}-(CH_2)_6-\overset{\phi}{CH_2}-\overset{\mathbf{c}}{CO}-NH-\overset{\beta}{CH_2}-(CH_2)_4-CO-$	c d β δ ϕ	179.86 179.56 43.54 43.91 33.88
B'-B' (Ny4,6-Ny4,6)	$-NH-(CH_2)_3-\overset{\theta}{CH_2}-NH-CO-\overset{\omega}{CH_2}-(CH_2)_2-\overset{\omega}{CH_2}-\overset{\mathbf{s}}{CO}-NH-\overset{\theta}{CH_2}-(CH_2)_2-\overset{\theta}{CH_2}-NH-CO-\overset{\omega}{CH_2}-(CH_2)_2-\overset{\omega}{CH_2}-CO-$	s θ ω	178.74 43.38 33.19
A-B' (Ny6- Ny4,6)	$-NH-(CH_2)_4-\overset{\varepsilon}{CH_2}-\overset{\mathbf{t}}{CO}-NH-\overset{\chi}{CH_2}-(CH_2)_2-\overset{\theta}{CH_2}-NH-CO-\overset{\omega}{CH_2}-(CH_2)_2-\overset{\omega}{CH_2}-CO-$	t χ θ ω	179.57 43.23 43.38 33.19
B'-A (Ny4,6-Ny6)	$-NH-(CH_2)_3-\overset{\theta}{CH_2}-NH-\overset{\mathbf{s}}{CO}-\overset{\omega}{CH_2}-(CH_2)_2-\overset{\omega}{CH_2}-\overset{\mathbf{e}}{CO}-NH-\overset{\tau}{CH_2}-(CH_2)_3-\overset{\varepsilon}{CH_2}-CO-$	e s τ θ ω	178.40 178.74 43.78 43.38 33.19

[a] A, B and B′ indicate the Ny6, the examethylene sebacate Ny6,10 and the Ny4,6 units, respectively.

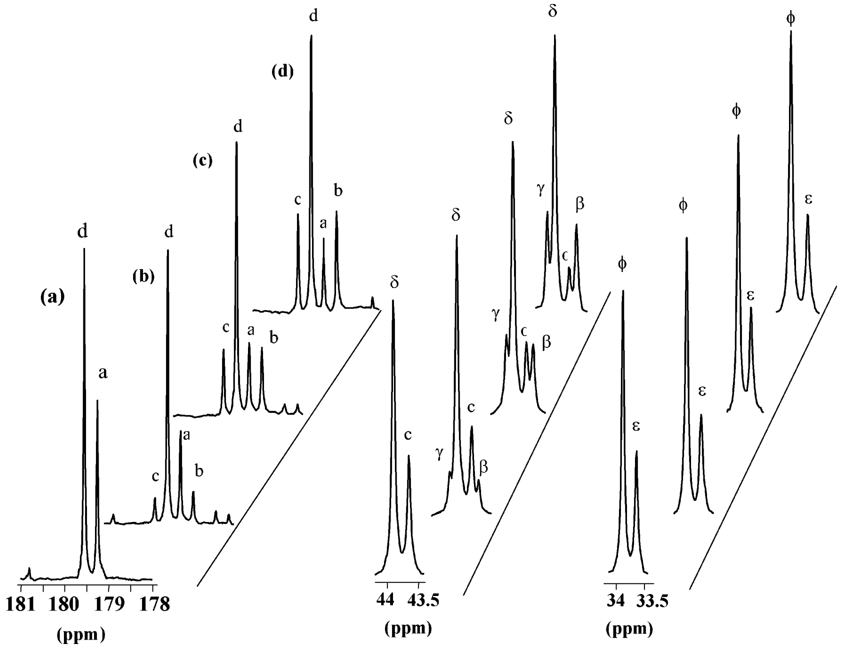


Figure 3. Portions of the ^{13}C NMR spectra of the Ny6/Ny610 melt mixed blends at 310 °C for 0 (a), 10 (b), 30 (c), and 60 (d) min. Chemical shifts and the assignments of the labled peaks are reported in Table 4.

the ^{13}C NMR spectra of the Ny6-COOH/Ny6,10 blends (Figure 3).

The ^{13}C NMR analysis is usually performed[23−28] by analyzing the copolyamide dyads (for instance, random copolymers with equimolar composition present an equal molar fraction (*F*) of AA, BB, AB, and BA sequences). This description was thought to be appropriate in the case of aliphatic polycondensation

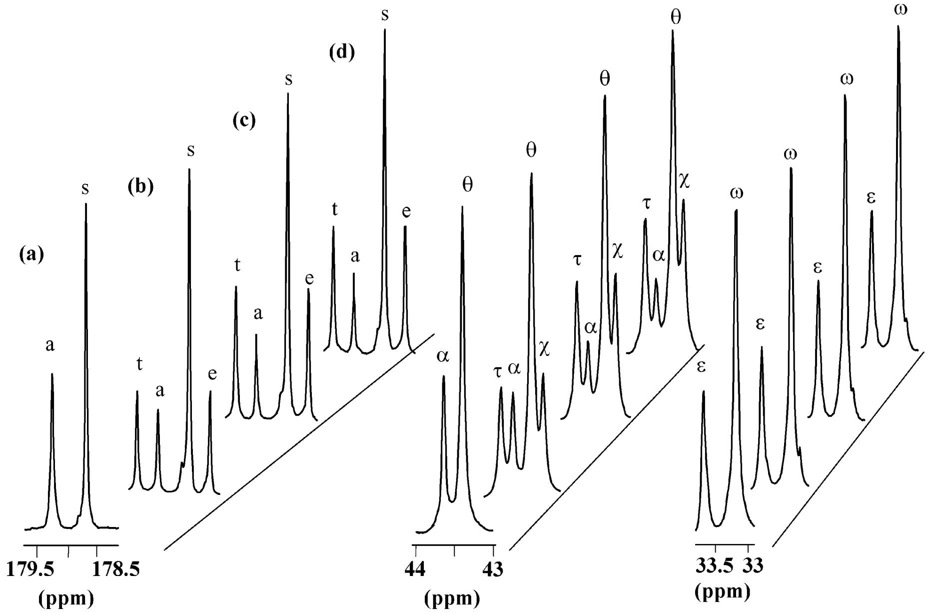


Figure 4. Portions of the ^{13}C NMR spectra of the Ny6/Ny4,6 melt mixed blends at 310 °C for 0 (a), 30 (b), 60 (c), and 120 (d) min. Chemical shifts and the assignments of the labeled peaks are reported in Table 4.

polymers, where the electronic transmission is quite poor and the ^{13}C chemical shift sensitivity generally does not go beyond dyads.[23−28]

Some workers[23−25] reported the structural characterization of Ny6 based copolyamides only in terms of the number-average block length, whereas for the copolyamides synthesized by melt mixing of Ny4,6-Ny6,I (I = poly(hexamethylene isophthalamide),[22] a complete structural characterization (i.e., molar sequence distribution of the dyads, their average sequence length and the degree of randomness) was made applying the statistical model of Devaux et al.,[9] which yields pertinent results when it is applied to copolymers from dicarboxyl acids and diamines or dialcohols (such as those from melt mixing of PC/PET, PC/PBT, Ny6I/Ny4,6, PET/PBT blends).[1,2,9,22]

However, this model does not apply to copolymers from dicarboxyl acids and lactames or lactones (i.e., Ny6/Ny6,6; Ny6/NY6,10; Ny6/Ny4,6; PCL/PET; PCL/PC; etc.), which lack of symmetry and cannot be divided into four symmetrical subunits. Since our systems fall in this second category, we have chosen to develop a different statistical model.

The sebacic moiety of Ny6,10 has two carbonyls in its repeat unit, whereas the Ny6 unit possesses only one carbonyl. Therefore, in the physical blend, the carbonyl signals of the Ny6,10 (peak d, Figure 3) have an intensity nearly doubled with respect to the carbonyl resonance due to the Ny6 units (peak a, Figure 3). As the exchange reaction proceeds the hetero-dyads Ny6-Ny6,10 (AB) and Ny6,10-Ny6 (BA) generate the new peaks b and c, respectively, showing always the same intensity.

The relative intensity of the four carbonyl peaks in Figure 3 does not change, in a first approximation, after 60 min of mixing at 310 °C indicating that the sequence distributions of the copolyamides is now constant, in agreement with the DSC and MALDI results (Tables 1 and 3).

The relative intensities of the carbonyl peaks were used to calculate the molar composition, the molar sequence distribution, the number-average sequence lengths and the degree of randomness of the copolyamides synthesized, using the eqs 1−8. The results are reported in Table 6. They show that all synthesized copolyamides have a molar composition very close to that of the initial physical blends, and that the segmented copolyamides formed at relatively low reaction time at 310 °C evolve quickly toward a random distributions of the dyad sequences, as the reaction time increases. The figures in Table 6 come in agreement with the data obtained by the MALDI analysis (Table 3).

To further validate the carbonyl peak assignments and understand their relative intensity in the ^{13}C NMR spectra of the copolyamides synthesized, we ought to note (Table 5) that, taking into account that sebacic acid has two carbonyls, the dyad A−A (Ny6-Ny6) generates one carbonyl signal of type a and another signal which can be of type a or b, depending if followed by A (Ny6) or B (Ny6,10) units along the chain sequence. In the same way, the dyad A−B generates two carbonyl signals of type b and d, and another signal which can be of type c or d, depending if followed by A or B units along the chain sequence. The dyad B−A generates two carbonyl signals of type d and c and another signal which can be of type a or b, depending if followed by A or B units along the chain sequence. The dyad B−B generates three carbonyl signals of type d and another signal which can be of type c or d, depending if followed by A or B units along the chain sequence.

According to chain statistics,[29,36] for an equimolar AB random copolymer, the four dyads, B−A (Ny6,10-Ny6), B−B (Ny6,10-Ny6,10), A−A (Ny6-Ny6), and A−B (Ny6-Ny6,10), should be present in equal amounts; thus we should expect (Table 5) a relative intensity of 1/3/1/1 for the signals c, d, a, and b, respectively, in reasonable agreement with the experimental data recorded for the Ny6-Ny6,10 copolymer obtained after 30 min at 310 °C (Figure 3). The same peak intensity distribution is observed for the methylene peaks in the region 43.5−44 ppm (Figure 3, Table 4). Looking at copolyamide sequences longer than dyads (the eight triads are reported in Table 5), the same relative intensity of 1/3/1/1 for the signals c, d, a, and b, is obtained for a random Ny6-Ny6,10 copolyamide, assuming that the eight triads have the same relative weight.

Table 5. Types of Carbonyl Resonance Signals Due to the Dyads and Triads Sequences[a] in the Ny6/Ny6,10 and in the Ny6/Ny4,6 Copolyamides[a]

	Sequences
	Dyads
A-A	$-\mathbf{NH-(CH_2)_5-\overset{a}{CO}-NH-(CH_2)_5-\overset{(a/b)}{CO}}-$
A-B	$-\mathbf{NH-(CH_2)_5-\overset{b}{CO}}-NH-(CH_2)_m-NH-\overset{d}{CO}-(CH_2)_n-\overset{(d/c)}{CO}-$
B-A	$NH-(CH_2)_m-NH-\overset{d}{CO}-(CH_2)_n-\overset{c}{CO}-\mathbf{NH-(CH_2)_5-\overset{(a/b)}{CO}}-$
B-B	$-NH-(CH_2)_m-NH-\overset{d}{CO}-(CH_2)_n-\overset{d}{CO}-NH-(CH_2)_m-NH-\overset{d}{CO}-(CH_2)_n-\overset{(d/c)}{CO}-$
	Triads
AAA	$-\mathbf{NH-(CH_2)_5-\overset{a}{CO}-NH-(CH_2)_5-\overset{a}{CO}-NH-(CH_2)_5-\overset{(a/b)}{CO}}-$
AAB	$-\mathbf{NH-(CH_2)_5-\overset{a}{CO}-NH-(CH_2)_5-\overset{b}{CO}}-NH-(CH_2)_m-NH-\overset{d}{CO}-(CH_2)_n-\overset{(d/c)}{CO}-$
ABA	$-\mathbf{NH-(CH_2)_5-\overset{b}{CO}}-NH-(CH_2)_m-NH-\overset{d}{CO}-(CH_2)_n-\overset{c}{CO}-\mathbf{NH-(CH_2)_5-\overset{(a/b)}{CO}}-$
BAA	$-NH-(CH_2)_m-NH-\overset{d}{CO}-(CH_2)_n-\overset{c}{CO}-\mathbf{NH-(CH_2)_5-\overset{a}{CO}-NH-(CH_2)_5-\overset{(a/b)}{CO}}-$
BBA	$-NH-(CH_2)_m-NH-\overset{d}{CO}-(CH_2)_n-\overset{d}{CO}-NH-(CH_2)_m-NH-\overset{d}{CO}-(CH_2)_n-\overset{c}{CO}-\mathbf{NH-(CH_2)_5-\overset{(a/b)}{CO}}-$
BAB	$-NH-(CH_2)_m-NH-\overset{d}{CO}-(CH_2)_n-\overset{c}{CO}-\mathbf{NH-(CH_2)_5-\overset{b}{CO}}-NH-(CH_2)_m-NH-\overset{d}{CO}-(CH_2)_n-\overset{(d/c)}{CO}-$
ABB	$-\mathbf{NH-(CH_2)_5-\overset{b}{CO}}-NH-(CH_2)_m-NH-\overset{d}{CO}-(CH_2)_n-\overset{d}{CO}-NH-(CH_2)_m-NH-\overset{d}{CO}-(CH_2)_n-\overset{(d/c)}{CO}-$
BBB	$-NH-(CH_2)_m-NH-\overset{d}{CO}-(CH_2)_n-\overset{d}{CO}-NH-(CH_2)_m-NH-\overset{d}{CO}-(CH_2)_n-\overset{d}{CO}-NH-(CH_2)_m-NH-\overset{d}{CO}-(CH_2)_n-\overset{(d/c)}{CO}-$

[a] A corresponds to the Ny6 units, B corresponds to the Ny6,10 or Ny4,6 units, for Ny6-Ny6,10 and Ny6-Ny4,6 copolymers, respectively. $m = 6$ and $n = 8$ for the Ny6,10 units; $m = 4$ and $n = 4$ for Ny4,6 units. Carbonyls **b**, **c**, and **d** correspond to the peaks **e**, **t**, and **s**, respectively, in the ^{13}C NMR spectra of the Ny6-COOH/Ny4,6 blends (Figure 4).

Table 6. Molar Composition Molar Fraction of Dyads Sequencs, Average Sequence Lengths and Degree of Randomness (B), Calculated from ^{13}C NMR Spectra of the Equimolar Ny6-COOH/Ny6,10 and Ny6-COOH/Ny4,6 Melt Mixed Blends, Using Eqs 1−7 (See Experimental Part)

melt mixing conditions		copolymer[1] composition	molar fraction of dyads[2]				average sequence lengths[3]		
T (°C)	t (min)	C_AC_B[2]	F_{AA}	F_{AB}	F_{BA}	F_{BB}	A−A	B−B	B_4
				Ny6/Ny6,10					
290	120	50/50	0.31	0.19	0.19	0.31	2.6	2.6	0.76
290	180	50/50	0.25	0.25	0.24	0.26	2	2	1.0
310	10	48/52	0.36	0.12	0.14	0.48	4.0	3.7	0.52
310	30	48/52	0.29	0.19	0.21	0.31	2.5	21.5	0.80
310	60	47/53	0.22	0.25	0.287	0.24	1.9	1.85	1.07
				Ny6/Ny4,6					
310	30	49/51	0.30	0.19	0.19	0.32	2.6	2.7	0.76
310	60	48/52	0.23	0.25	0.26	0.25	1.9	2.0	1.02
310	120	48/52	0.23	0.25	0.27	0.25	1.9	1.9	1.08

In Figure 5a−d are compared the experimental and calculated ^{13}C NMR spectral intensities of the carbonyl peaks corresponding to the Ny6/Ny6,10 copolyamides obtained after 30 and 60 min heating at 310 °C. As observed above, the experimental intensities of the carbonyl peaks of the blend melt mixed 30 min (Figure 5a), come very close to those calculated for the random copolyamide (Figure 5b). However, the random distribution of sequences appears a bit altered for the blend melt mixed for 60 min (Figure 5c). Analyzing the spectra of the Ny6-Ny6,10 copolyamides obtained after 60 min heating at 310 °C (Figure 3c), it can be observed that the intensity of peaks c (dyads B−A) and b (dyads A−B) is higher with respect to peak a. The relative intensity of peaks c, d, a and b is now 1/3/0.7/1 (Figure 5c), slightly different from that seen above for a random Ny6-Ny6,10 copolyamide (1/3/1/1, Figure 5b). These results could be tentatively interpreted looking at the triads reported in

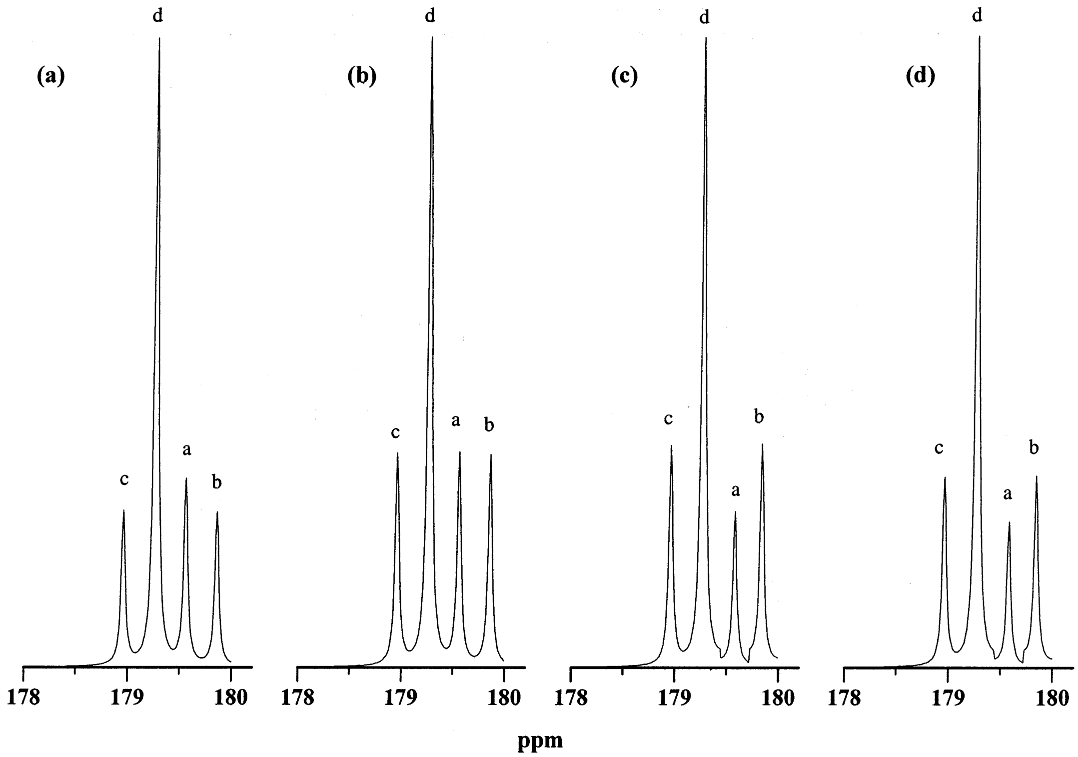


Figure 5. Experimental (a) and calculated (b) ^{13}C NMR spectra of Ny6-COOH/Ny6,10 blends reacted at 310 °C for 30 min. Experimental (c) and calculated (d) ^{13}C NMR spectra of Ny6-COOH/Ny6,10 blends reacted at 310 °C for 60 min.

Table 5, assuming that the weight of hetero-triads AAB, BAA, BBA, ABB, ABA, BAB is higher than that of the homo-triads AAA and BBB. We have assumed the probability of AAB 14.5%, BAA 14.5%, BBA 14.5%, ABB 14.5%, ABA 14.0%, BAA 14.0%, AAA 7.0% and BBB 7.0%, to obtain a relative intensity of carbonyls 1/3.4/0.8/1, which reflect the experimental finding (Figure 5c,d). This result confirms the above ^{13}C NMR carbonyl peaks assignments

Using these triads abundances, an average sequence length of 1.7 was also calculated for the AA and the BB dyads, in fair agreement with data in Table 6.

These results are even in better accord with those obtained by MALDI analysis of Ny6-N6,10 and Ny6-Ny4,6 copolyamides at longer reaction time (Table 3). This interpretation implies that in the copolyamides obtained at longer reaction time the weight of the alternating sequences (ABA and BAB) prevails and that the exchange reactions (Scheme 1) goes a bit beyond the formation of random copolymer. This result may be due to the high concentration of reactive carboxyl groups.

Conclusions

This paper reports results that appear important under a double aspect. From one side, it shows how *facile* is the high yield synthesis of random copolyamides via the melt mixing of the corresponding polyamides. What makes the synthesis so *facile* is the use of a carboxyl terminated polyamide (Ny6-COOH) to attack the other polyamide (Ny4,6 or Ny6,10), as described herewith. The DSC data acquired provide a clear picture of the process. The second relevant point is about the sequence analysis of the copolyamides, made using their ^{13}C NMR spectra. The sequence has been derived directly from chain statistics principles, avoiding the use of inadequate procedures. To our knowledge, this is the first time as far as condensation copolymers are concerned.

Interestingly, the sequence analysis of our copolyamides has been also performed independently, by extracting pertinent information from their MALDI spectra. The results have been found in excellent agreement with those from ^{13}C NMR

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Supporting Information Available: Figure 1S, reporting an enlarged section of the MALDI spectra of the Ny6-COOH/Ny46 blends melt mixed at 310 °C for (a) 30, (b) 60, and (c) 90 min, where peaks labeled $L_{x,y}$ indicate linear oligomers whereas $R_{x,y}$ indicate cyclic oligomers. This material is available free of charge via the Internet at http://pubs.acs.org.

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