Exchange Reactions Occurring through Active Chain Ends. MALDI−TOF Characterization of Copolymers from Nylon 6,6 and Nylon 6,10

Concetto Puglisi and Filippo Samperi

Istituto per la Chimica e la Tecnologia dei Materiali Polimerici, Consiglio Nazionale delle Ricerche. Viale A. Doria, 6-95125 Catania, Italy

Sabrina Di Giorgi and Giorgio Montaudo*

Dipartimento di Scienze Chimiche, Università di Catania. Viale A. Doria, 6-95125 Catania, Italy

Received August 19, 2002; Revised Manuscript Received November 27, 2002

ABSTRACT: A study on the sequence and composition of copolyamides formed by activated exchange reactions occurring in the melt mixing of Ny6,10 and Ny6,6 is reported. Equimolar mixtures of Ny6,10, Ny6,6, and carboxyl-terminated Ny6,6 (Ny6,6-COOH) samples were melt mixed at different temperatures (290−310 °C) for different times (10−180 min). The determination of copolyamides formation, sequence, and composition proved to be unfeasible with ^{13}C NMR spectroscopy. On the other hand, matrix-assisted laser desorption ionization−time-of-flight (MALDI−TOF) mass spectra allowed the detection of the copolyamides formation and the determination of their sequence and composition. The results can be reconciled within the overall scheme of exchange reaction occurring through active chain ends. In fact, the composition of the copolyamides formed by the exchange of Ny6,6-COOH/Ny6,10 mixtures showed a higher amount of Ny6,6 units, with respect to the initial blends composition, and a higher value of the Ny6,6 average block length, at the beginning of the reaction (10 min). The composition of the copolyamides was found to be equal to the feed composition (50/50), after 30 min of heating, with a random distribution of sequences. The composition and the sequence distributions of the copolyamides remained unaffected even at a higher heating time (180 min) although some degradation reactions also occurred. Instead, the exchange reaction of a mixture of high molar mass Ny6,6 and Ny6,10 both containing a very low amount of carboxylic chain ends produced a segmented copolyamides even at high heating time (150 min). The Ny6,6/Ny6,10 copolyamides were also characterized by differential scanning calorimetry (DSC) and by wide-angle X-ray spectroscopy (WAXS).

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.[1−7]

Interchange 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.

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.[7−10]

These exchange processes are important also from the synthetic point of view, since it will be possible to design tailored block or random copolymers with potential useful properties. In fact, the synthesis of copolymers from reactive blending of homopolymers has now become a convenient route, alternative to the usual copolymerization reactions that start from monomers.[1,11−13]

Amide−amide exchange reactions are not observed at temperatures below 320 °C (processing temperature), so that only amidolysis or acidolysis processes do occur.[10,14−17]

In the present case, we report on the reactive melt-mixing process of low molar mass nylon 6,6 terminated with a high amount of carboxyl chain ends (namely Ny6,6-COOH) and high molar mass nylon 6,10, since only carboxyl chain ends proved to be reactive.[18]

To have a control on the exchange reactions occurring in the molten state it is important to know whether the resulting product is actually a block copolymer, a random copolymer, or a mixture of two homopolymers.

The determination of the composition and of the average block length of copolyamides is usually performed by ^{13}C NMR, which is possible when the polyamides are dissolved in sulfuric acid or fluorosulfonic acid. In fact, the carbonyl signal resonances of copolyamides become sensitive to chain sequences and can be analyzed in terms of dyad sequences.[19−23]

However, up to the present time, the literature has reported that ^{13}C NMR signals due to carbonyls of Ny6,6/Ny6,10 copolymers cannot be resolved,[24] and therefore, the composition and the sequence of these copolyamides cannot be determined by this technique.

The determination of sequence and composition in copolymers having large comonomer subunits can be often achieved by mass spectrometry (MS),[1,4,26−28] which is complementary and sometimes alternative to NMR analysis. In particular, in the past decade the MS analysis of polymers has taken advantages from the recent development of the matrix-assisted laser desorption ionization−time-of-flight (MALDI−TOF) MS which is a soft ionization technique that possesses high

* Corresponding author. E-mail: gmontaudo@dipchi.unict.it.

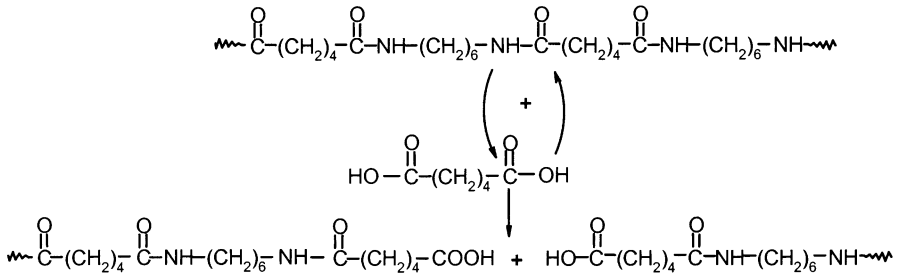
10.1021/ma021348c CCC: $25.00
Published on Web 01/17/2003

Table 1. Thermal Characteristics of Ny6,10 and Ny6,6-COOH Homopolymers and of Their Equimolar Blends Melt Mixed for Different Times at 290 °C, As Derived from Their DSC Curves, Where T_g = Glass Transition Temperature, T_m = melting Temperature, and ΔH_m = Normalized Enthalpy of Melting

sample	homopolymers and blends	reaction time (min)	T_g (°C)	T_m (°C)	ΔH_m (J/g)	$(\Delta H_m)_{tot}$[a] (J/g)	% C[b]
1	Ny610		70	221	61.8		30.80
2	Ny66COOH		48	258	61.5		29.90
3	Ny610/Ny66COOH		46; 69	220; 243	35.3; 18.4	53.7	26.45
4	Ny610/Ny66COOH	5	47; 68	217; 242	36.8; 20	56.8	27.97
5	Ny610/Ny66COOH	10	48; 65	210; 237	29.4; 10	39.4	19.40
6	Ny610/Ny66COOH	15	51; 62	208; 233	13.0; 13.26	29.26	14.41
7	Ny610/Ny66COOH	30	60	196		54.2	26.70
				192; 207[c]	17.3; 16.8[c]	34.1	16.80
8	Ny610/Ny66COOH	60	59	196		56.9	28.00
				192; 205[c]	19.3; 6.7[c]	26	12.80
9	Ny610/Ny66COOH	180	59	193		46.5	22.90
				192; 205[c]	19.6; 5.3[c]	24.9	12.26

[a] $(\Delta H_m)_{tot}$ is the sum of the ΔH_m determined at each melting processes observed in the DSC curves. [b] The % of crystallinity of the homopolymers were calculated using specific heats of fusion for 100% crystalline Ny6,6 ($\Delta H°_m$ = 200.35 J/g) and Ny6,10 ($\Delta H°_m$ = 205.75 J/g) samples.[31] The crystallinity of all blends are calculated for an average value (203.05 J/g) of the $\Delta H°_m$ of Ny6,6 and Ny6,10 samples. [c] Determined in the second heating run (see Experimental Section).

Scheme 1



sensitivity and allows desorption and ionization of intact polymer molecules and their identification as mass resolved polymer chains.[27,28] The intensities of the peaks appearing in the mass spectrum of a copolymer is directly bound to the relative abundance of oligomers present in the copolymer and reflects the composition and sequence distributions in the copolymer. 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 approached, providing a new method for deducing the sequence distributions and composition of comonomers in copolymers by MS techniques.[4,25] Chain statistics (Bernoullian or first- or second-order Markoffian) allows the characterization of any arrangement of comonomer units along the chain and the possibility of building theoretical mass spectra. By comparison of theoretical and experimental mass spectra of a given copolymer, the composition and sequence distributions can be obtained. The MS method has been successfully applied to the characterization of several copolymer systems.[25−28] and also to the characterization of the copolyesters obtained from polyester/polyester blends.[4]

In this work, the MALDI−TOF spectra of the products obtained form the reactive melt-mixing at 290 °C of Ny6,6 and Ny6,10 allowed the characterization of end groups of homopolymers and copolymers and also the determination of composition, sequence distribution, average sequence length, and degree of randomness of the Ny6,6/Ny6,10 copolyamides.

Experimental Section

Materials. Basic materials were purchased from Aldrich Chemical Co. Adipic acid (AA), diphenylsulfone (DPSO), trifluoroethanol (TFE), *m*-cresol, formic acid (HCOOH), fluorosulfonic acid (FSO_3H), 2-(4-hydroxyphenylazo)benzoic acid (HABA), and potassium iodide (KI) were used as supplied. Ny6,6 and Ny6,10 samples, both acquired from Aldrich Chemical Co., were powdered by mechanical grinding in the presence of solid CO_2 and dried at 80 °C, under vacuum, for 1 week.

Viscometry. Solution viscosities were measured at 30 ± 0.1 °C in *m*-cresol with a Ubbelhode viscometer ($[\eta] = \eta_{spec}/C$; C = 0.5 g/dl). The following values were obtained: Ny6,6, $[\eta]$ = 1.72; N6,6-COOH, $[\eta]$ = 0.54; Ny6,10, $[\eta]$ = 3.2. On the basis of these data, average viscometry molar masses (M_v) of the Ny6,6, Ny6,6-COOH and Ny6,10 samples were calculated using specific the Mark−Houwink coefficients (K and α):[31] for Ny6,6 and Ny6,6-COOH samples, $K = 240 \times 10^{-3}$ mL/g and α = 0.61; for Ny6,10, sample $K = 13.5 \times 10^{-3}$ mL/g and α = 0.96. Calculated M_v values for the homopolyamides used in this study are as follows: Ny6,6 M_v = 48 000 g/mol; N6,6-COOH M_v = 7200 g/mol; Ny6,10 M_v = 36 100 g/mol.

Synthesis of Dicarboxyl-Terminated Ny66. A Ny6,6 sample containing carboxyl groups at both ends (Ny6,6-COOH; sample 2, Table 1) was prepared by acidolysis of high molar mass Ny6,6 (M_v = 48 000 g/mol) with adipic acid (Scheme 1) in a molar ratio 1/0.15, in DPSO at 245 °C for 30 min, under N_2 flow.

Typically, 10 g (44.19 mmol) of Ny66 and 15 g of DPSO were melted in a three necked round-bottom flask, at 245 °C under stirring. Then, 967.76 mg (6.629 mmol) of adipic acid was added, and the mixture was reacted for 30 min. After cooling, the mixture was washed several times with acetone, and the solid residue was dried at 60 °C under vacuum for 3 days.

Detection of Amino and Carboxylic End Groups. The concentration of amino terminal groups, and carboxylic chain ends in Ny6,6 and Ny6,10 samples were determined by the procedure described in the literature.[29,30] Specific values (mmol/kg) for the samples used in this study are as follows: for Ny6,6, $[NH_2]$ = 37, [COOH] = 9; for Ny6,10, $[NH_2]$ = 15, [COOH] = 42; for Ny6,6-COOH, $[NH_2]$ = 0.5, [COOH] = 310.

Melt-Mixing Process. Mixtures of high molar mass Ny6,6 and Ny6,10 and high molar mass Ny6,10 with Ny6,6-COOH

were heated at 290 °C in the presence of DPSO to reduce melt viscosity.

Next, 2 g each of equimolar mixtures of Ny6,10 and Ny6,6-COOH samples (Ny6,10/Ny6,6 55/45 w/w ratio), with respect to the repeat unit, with 30% DPSO, was placed in a glass reaction vessel and reacted under a stream of N_2, stirring at 290 °C, for different times (5−180 min). The Ny6,6-COOH/Ny6,10 mixtures were also reacted at 310 °C for 5, 30, and 60 min. The melt mixing of equimolar mixtures of both high molar mass Ny6,6 and Ny6,10 samples was carried out at 290 °C for 150 min. Each mixture, thus obtained, was dissolved in formic acid and precipitated in water. The resultant precipitates were collected and washed several times with acetone at room temperature in order to remove all DPSO and then dried at 60 °C under vacuum for 2 days.

NMR Spectroscopy. ^{13}C NMR spectra were obtained on 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; 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.

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 20−25 kV, and 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) was 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 co-crystallization.

DSC Measurements. The thermal properties (T_g and T_m) of all samples in Table 1 were determined by an indium-calibrated Mettler DSC 20 instrument, in a dry nitrogen atmosphere. Separate measurements were carried out on about 10−15 mg of each sample to determine the glass transition (T_g) and the melting point (T_m) values. Values reported in Table 1 represent the average of several runs ($\Delta T = \pm 1$ °C). T_g values were determined at heating rate of 5 °C/min in the range 25−100 °C, while the T_m values were obtained at a heating rate of 10 °C/min, in the range 100−300 °C (first and second heating run).

To check if the melting point profiles observed in the first heating run were subjected to change after annealing, all samples were annealed in the DSC apparatus for 5 min at the temperature corresponding to the maximum of their melting curve. Then the samples were left to cool and were scanned as in the first scan.

X-ray Analysis. wide-angle X-ray diffraction (WAXD) spectra were obtained at room temperature by means of a Bruker D5005 operating at 40 kV and 30 mA, using Cu Kα radiation ($\lambda = 1.5406$ Å). Data were collected in the range 5−50° (2θ).

MACO4 Calculation. MALDI−TOF MS data were analyzed by using the MACO4 program previously described.[4,25] 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 or nonselective cleavage process. The program generates the theoretical mass spectrum using the equation $I_{A_mB_n} = f(P_{AA}, P_{AB}, P_{BA}, P_{BB})$, where $I_{A_mB_n}$ is the intensity of the mass peak corresponding to a A_mB_n oligomer, and P_{ij} describes the probability of finding the component i after the component j.

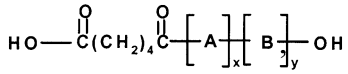
If a best fit is requested, the computer code varies the parameters associated with the selected mathematical model until it finds the best match between the observed and calculated data. MACO4 yields as output the parameters that give the best agreement and a listing of the corresponding to theoretical spectrum. The difference between observed and calculated values is expressed in terms of error by means of the Hamilton agreement factor[25] (AF): $AF = q\sum_i(I_i^{exptl} - I_i^{calcd})$,[2] where I_i^{exptl} and I_i^{calcd} are the normalized experimental and calculated abundances of the oligomers and where the normalized factor q is given by $q = 1/(\sum_i(I_i^{exptl})^2)^{0.5}$.

By means of this program, the sequence distributions, composition, average sequence length, the degree of randomness and extent of exchange of the Ny6,6/NY6,10 copolyamides prepared by melt mixing of the corresponding homopolyamides can be obtained. Pertinent values are reported in Table 3.

Table 2. Assignments of the Peaks Observed in the MALDI Spectra of the Ny6,6-COOH/Ny6,10 Melt Mixed Blends Reported in Figure 5[a]

		normalized intensity of the peaks observed at different mixing times:				
oligomer	$[M + K]^+$ mass	10 min	15 min	30 min	60 min	180 min
A_3	864.1	100	100	63	53	46
A_2B	920.2	35	54	97	87	72
AB_2	976.3	30	48	100	100	100
B_3	1032.4	28	46	75	63	69
A_4	1090.4	95	88	47	33.5	28
A_3B	1146.5	35	41	71	58	55
A_2B_2	1202.6	25	39	85	82	86
AB_3	1258.7	22	32.5	72	72	75
B_4	1314.8	n.d.	35	46	41	47
A_5	1316.7	74	68	43	n.d.	24
A_4B	1372.8	31	43	50	42	43
A_3B_2	1428.9	20	31	63.5	60	63
A_2B_3	1485	18	27	63	65	72
AB_4	1541.1	n.d.	n.d.	48	48	54
B_5	1597.2	n.d.	n.d.	26	n.d.	26
A_6	1543	61	53		n.d.	n.d.
A_5B	1599.1	22	35	41	32	36
A_4B_2	1655.2	25	36	47	43	50
A_3B_3	1711.3	16	24	47	54	63
A_2B_4	1767.4	n.d.	21	41	50	60
AB_5	1823.5	n.d.	n.d.	35	33	40
B_6	1879.6	n.d.	n.d.	n.d.	n.d.	n.d.
A_7	1769.3	48	44	n.d.	n.d.	n.d.
A_6B	1825.4	22	28.5	n.d.	n.d.	n.d.
A_5B_2	1881.5	21	29.5	34	33	43
A_4B_3	1937.6	20	27.5	41	43	53
A_3B_4	1993.7	n.d.	19	41	47	54
A_2B_5	2049.8	n.d.	18	33	36	47
AB_6	2105.9	n.d.	n.d.	n.d.	n.d.	n.d.
B_7	2162	n.d.	n.d.	n.d.	n.d.	n.d.
A_8	1995.6	38	35	n.d.	n.d.	n.d.
A_7B	2051.7	18	24	n.d.	n.d.	n.d.
A_6B_2	2107.8	16	25	30	27	38
A_5B_3	2163.9	16	22	34	34	41
A_4B_4	2220	n.d.	n.d.	35	40	51
A_3B_5	2276.1	n.d.	n.d.	33	38	44
A_2B_6	2332.2	n.d.	n.d.	24	28	37
AB_7	2388.3	n.d.	n.d.	n.d.	n.d.	n.d.
B8	2444.4	n.d.	n.d.	n.d.	n.d.	n.d.

[a] Species corresponding to the following structure,



where A and B are Ny66 and Ny610 units, respectively.

Results and Discussion

The exchange reactions were carried out at 290−310 °C by mixing an equimolar mixture of high molar mass

Table 3. Results of the Analysis of MALDI−TOF Spectra of Ny6,6-COOH/Ny6,10 and Ny6,6/Ny6,10 Melt-Mixed Blends Using the MACO4 Program

heating time (min)	**P** matrix[a] ($P_{AA}/P_{AB}/P_{BA}/P_{BB}$)	extent of exchange[a]	composition[a] $C_{Ny6,6}/C_{Ny6,10}$	degree of randomness[a]	av. sequence length[a] $n_{Ny6,6}/n_{Ny6,10}$	agreement factor[a]
10	0.75/0.25/0.40/0.60	70	62/38	0.70	4.0/2.5	20
15	0.7/0.3/0.43/0.57	73	59/41	0.73	3.3/2.3	20
30	0.60/0.40/0.40/0.60	80	50/50	0.80	2.5/2.5	11
60	0.58/0.42/0.40/0.60	81	49/51	0.82	2.4/2.5	11
180	0.57/0.43/0.4/0.51	83	48/52	0.83	2.3/2.5	14
150[b]	0.81/0.19/0.24/0.76	43	56/44	0.43	5.3/4.1	20

[a] Calculated according to ref 25. [b] Mixture of high molar mass Ny6,6 and Ny6,10 with a low amount of carboxyl chain ends.

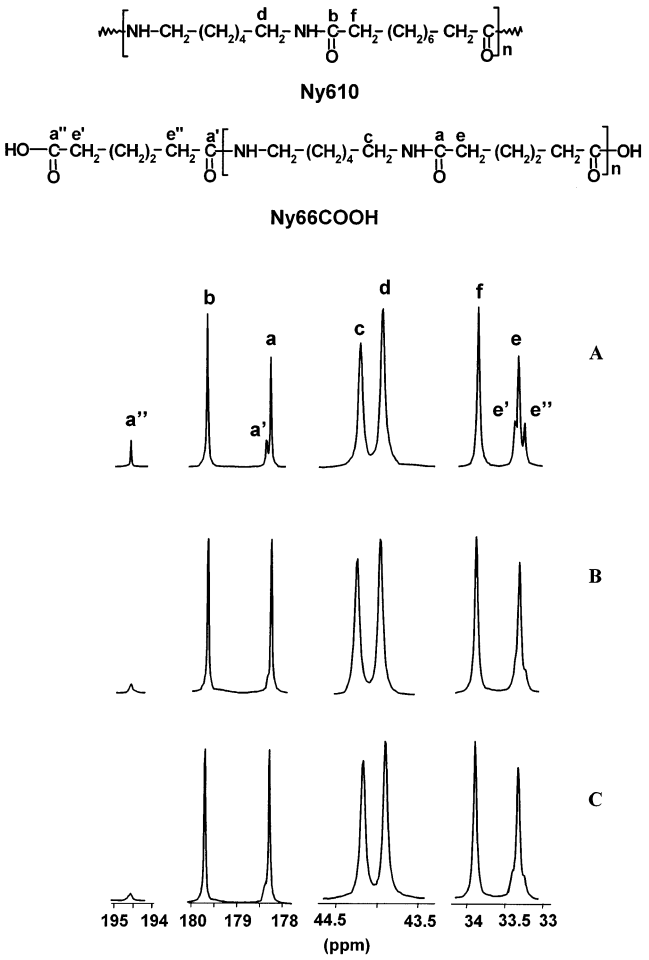


Figure 1. ^{13}C NMR spectra of Ny6,6-COOH and Ny6,10 equimolar mixtures: (a) physical blend; (b) blend melt mixed at 290 °C for 3 h; (c) blend melt mixed at 310 °C for 1 h.

Ny6,10 with high molar mass Ny6,6 or with a Ny6,6-COOH sample, under nitrogen atmosphere, up to 180 min. Dilution of the polymer blend with diphenyl sulfone (DPSO) proved to be useful in bringing the two homopolymers in close contact, leading the reaction to completion in relatively short heating times (Table 1).

In Figure 1 are shown the relevant portions of the ^{13}C NMR spectra of an equimolar mixture of low molar mass Ny6,6-COOH and high molar mass Ny6,10, either the physical blend and the melt-mixed blends at 290 °C and 310 °C for 180 and 60 min, respectively. Pertinent peak assignments are also reported in Figure 1. The carbonyl region at 195−178 ppm shows a decrement of the signals at 194.6 ppm due to the carboxyl end groups in Ny6,6 (peak a″ in Figure 1), when going from the physical blend (Figure 1a) to the melt-mixed blend (Figure 1b,c). The methylene regions at 44.5−33 ppm show similar minor changes.

In agreement with the literature data,[24] we found that from the analysis of the ^{13}C NMR spectra reported above it is not possible to deduce significant change after heating the blend, neither to deduce the formation of Ny6,6/Ny6,10 copolymers. On the other hand, the MALDI mass spectra of the mixture (see below) clearly show the formation of Ny6,6/Ny6,10 copolymers upon melt mixing of the two homopolymers.

In Figure 2 is given the MALDI spectrum of the low molar mass Ny6,6-COOH polymer used in our experiments. The most abundant peak series, assigned in the inset, correspond to linear oligomers terminated by carboxylic groups at both ends. Peaks due to cyclic oligomers are also present with low intensity.

In Figure 3 is shown the MALDI spectrum of the high molar mass Ny6,10 sample, together with the respective peak assignments. Cyclic oligomers appear to be the most abundant in the low-mass region reported in Figure 3 (1000−5000 Da), followed by linear oligomers with carboxyl and amino end groups.

In Figure 4 are shown the MALDI spectra of an equimolar mixture of low molar mass Ny6,6-COOH and high molar mass Ny6,10, either for the physical blend (Figure 4a) and for the melt-mixed blends at 290 °C for 30 min (Figure 4b). Ny6,6-COOH oligomers predominate in the low-mass region reported in Figure 4a (1000−5000Da), since the high molar mass Ny6,10 sample used here has very few oligomers in this region. A drastic change can be observed in the MALDI spectrum of the heated blend at 290 °C for 30 min (Figure 4b), hinting that the formation of Ny6,6/Ny6,10 copolymers by exchange reactions has occurred. In fact, the most intense peaks (Table 2) are due to copolymer oligomers terminated with acid end groups at both ends (species □), formed in the process of melt mixing.

The exchange reactions occurring in the melt mixing at 290 °C were followed as a function of time, and expanded portions of the MALDI spectra corresponding to the equimolar Ny6,6-COOH/Ny6,10 blend heated at different times are shown in Figure 5a−c. In the blends molten for 10 and 15 min at 290 °C (Figure 5, parts a and b), it can be noticed that oligomers having a copolymer structure are already present, but the Ny6,6 homooligomers are still predominant. However, in the blend molten for 30 min (Figure 5c) the peaks belonging to copolymers are the most intense. In this case, the intensity distribution of the peaks corresponding to the dimers, tetramers, pentamers, and examer oligomers (Figure 5c) is very similar to that expected for random A/B copolymers with an equimolar composition of the two comonomers.[28] This result implies that the exchange reaction has gone to completion.

The composition and the sequential arrangement of comonomer units present in the copolymers can be deduced from the relative intensity of the mass spectra peaks.[4,25,27,28] The MACO4 program was employed to

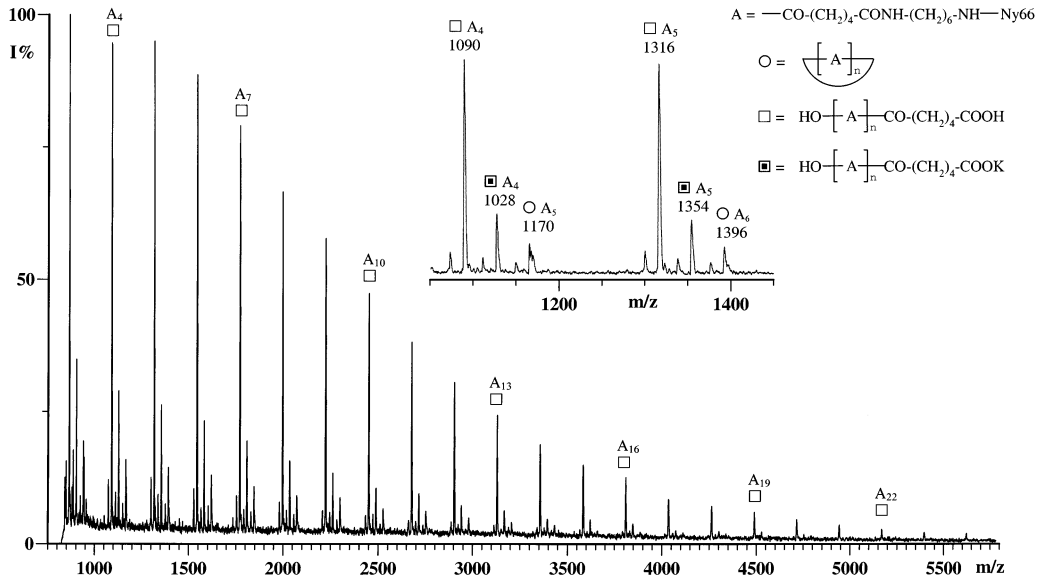


Figure 2. MALDI−TOF mass spectrum of Ny6,6-COOH sample.

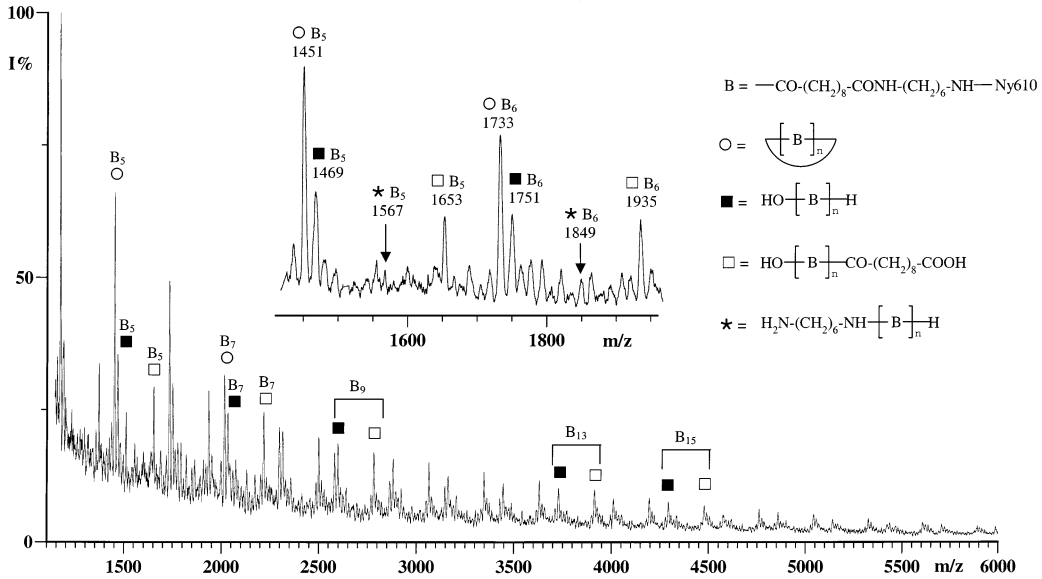


Figure 3. MALDI−TOF mass spectrum of high molar mass Ny6,10 sample.

simulate the experimental data and to characterize the sequence distribution of Ny6,6/Ny6,10 copolyamides,[4,27,28] using the normalized intensity of the peaks corresponding to the copolyamides, reported in Table 2.

To obtain a reliable composition of Ny6,6/Ny6,10 copolyamides, the calculations were performed excluding the intensities of pure A_n and B_m peaks appearing in Figure 5, parts a−c. In fact, the presence of Ny6,6 or Ny6,10 oligomers belonging to unreacted Ny6,6 and Ny6,10 chains might contribute to the intensity of these peaks.[4,27,28] The results of the calculations obtained by the MACO4 program are collected in Table 3. It can be noted that the copolyamide contains 64 mol % of Ny6,6 after 10 min heating and 59 mol % of Ny6,6 after 15 min. After 30 and 60 min heating, the copolyamides have compositions close to that of the initial blend composition i.e.: 50/50 (mol/mol), as expected for an exchange process carried out to completion.[1,2,4] The extent of exchange and the degree of randomness are very high (Table 3) even at lower heating time (10 min), indicating a high rate of exchange and the formation of a random copolyamide, due to the presence of a high concentration of reactive carboxyl chain ends. These results can be reconciled within the overall scheme of exchange reaction occurring through active chain ends.[1]

When an equimolar mixture of high molar mass Ny6,6 and Ny6,10 bearing a low concentration of carboxyl chain ends (see Experimental Section), was melt mixed at 290 °C for 150 min, a copolyamide with a molar composition of 54/46 was generated (Table 3). The extent of exchange of 43%, a degree of randomness of 0.43, and an average sequence length of 5.3/4.1 (Ny6,6/Ny6,10) clearly indicate the formation of a segmented copolyamide.

The above results are of particular interest, because they confirm that in this specific exchange process (Scheme 2), the copolymer composition is dependent on the extent of reaction, as expected in the case of a reactive melt-mixing process where only one of the two homopolymers has reactive chain ends.[1,2]

The above results suggest that the copolyamide is generated through an exchange process between Ny6,6 and N6,10 samples involving a fast acidolysis reaction (Scheme 2). As depicted in Scheme 2, at the beginning

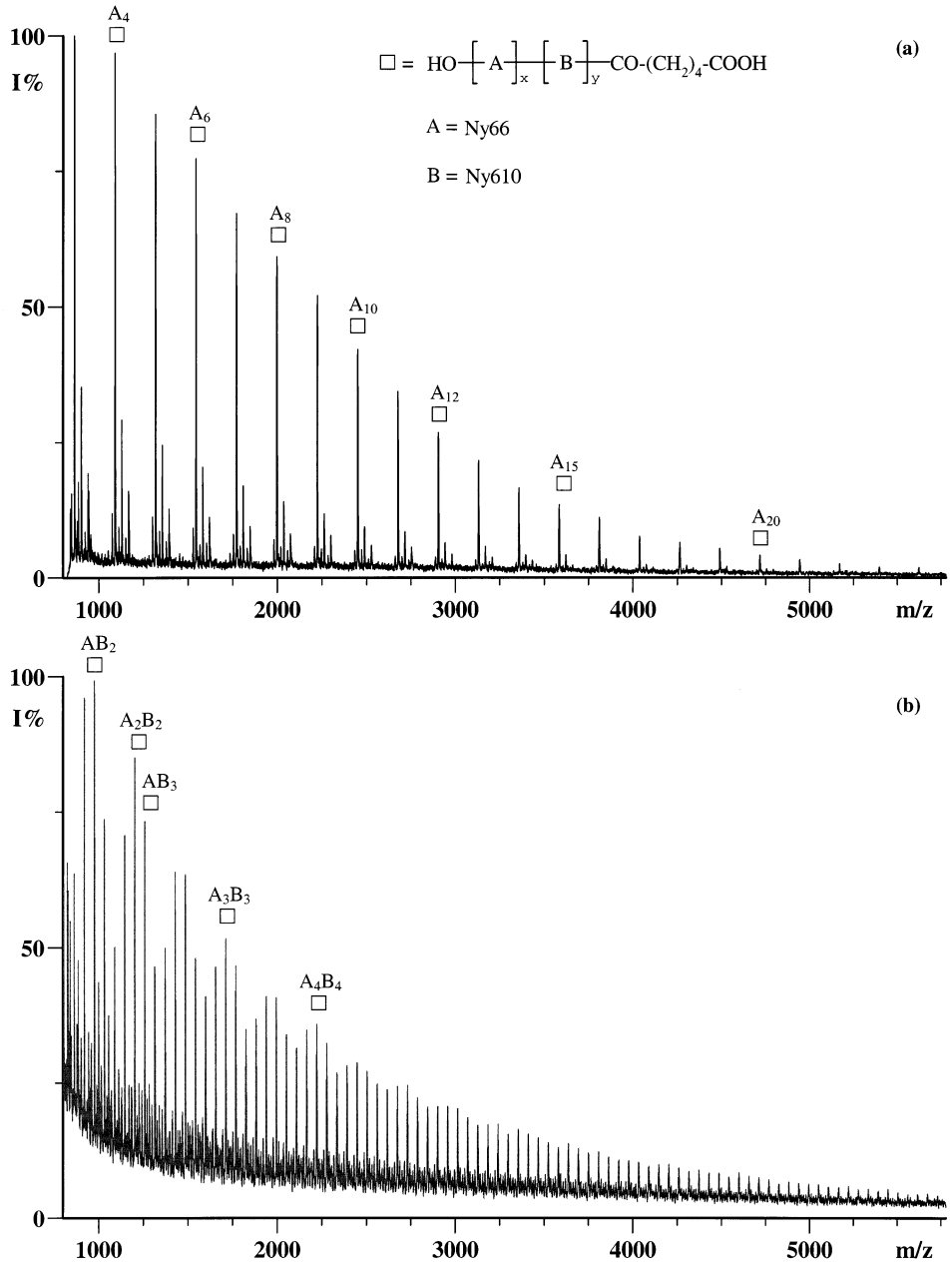


Figure 4. MALDI−TOF mass spectra of an equimolar mixture of Ny6,6-COOH (M_v = 7200) and high MM Ny6,10 (M_v = 36 100): (a) physical blend; (b) blend melt mixed at 290 °C for 30 min.

of the exchange process the carboxyl end groups of Ny6,6 attack the inner amide groups of Ny6,10, thus generating the copolyamide Ny6,6/Ny6,10 chains, plus lower molar mass Ny6,10 chains terminated with sebacic acid. The latter, in turn, can attack Ny6,6 molecules to produce further copolymer chains having a random sequence.

The reaction in Scheme 2 also predicts that the number of carboxyl end groups is not depleted in the course of the exchange reaction and therefore this can go to completion, producing a random copolyamide with the same composition of the initial homopolymers mixture.

If the reaction is carried out for longer times at 290 °C, further changes are observed in the MALDI spectra.

In parts a−c of Figure 6 are reported the MALDI spectra corresponding to melt-mixing times of 30, 60, and 180 min at 290 °C, respectively, in which can be identified mass peaks (Δ labeled) that can be assigned to the copolyamide chains terminated with the cyclopentanone units. These peaks are growing in intensity with the heating time and are due to the thermal decomposition reactions that take place at longer heating times. Intense peaks due to the co-oligomers terminated with cyclopentanone units were also observed in the MALDI spectra (not reported here for brevity) of the Ny66-COOH/Ny6,10 blends melt mixed at 310 °C for 10 min, and their intensities increase as the reaction time increases. In Scheme 3 is reported the thermal decomposition reaction of Ny6,6, which is known to generate cyclopentanone end chain units.[32] Since this thermal degradation reaction (Scheme 3) is due specifically to the adipic unit contained at the ends of copolymer chains, the amount of intact Ny6,6 units in the copolymer decreases, causing an increase of the molar composition of Ny6,10 units (Table 3).

In Figures 7 and 8 are shown the DSC traces corresponding to the polyamide mixtures investigated,

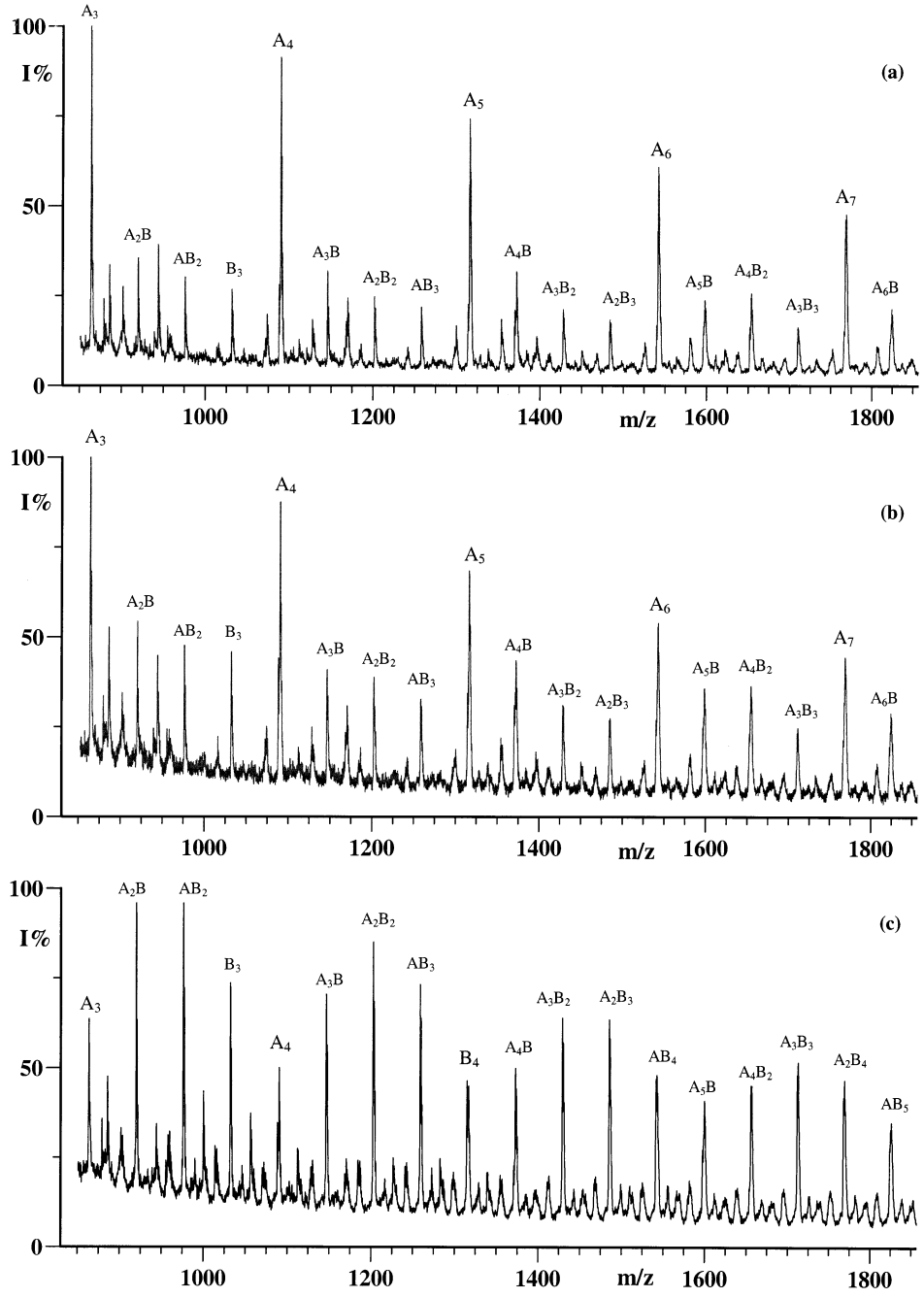
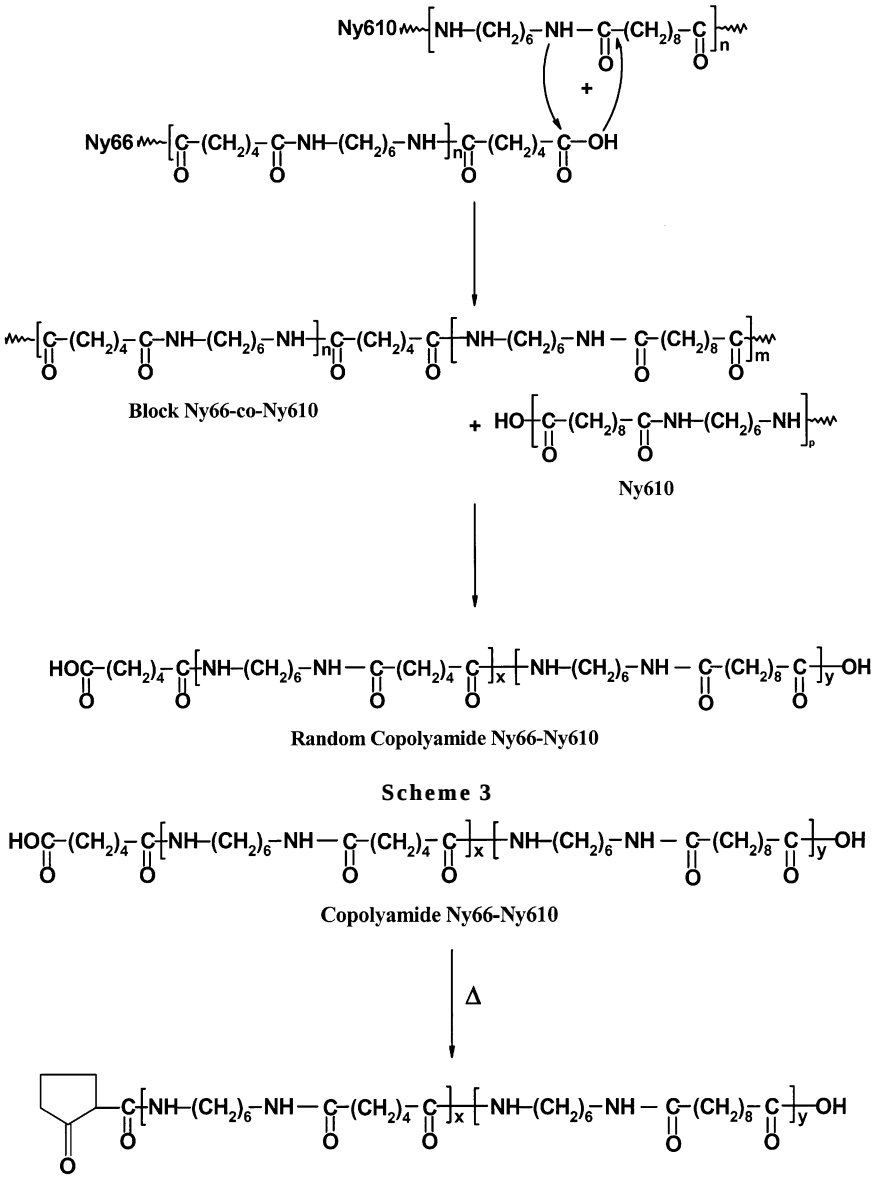


Figure 5. MALDI−TOF mass spectra, in the mass range 850−1850 Da, of equimolar Ny6,6-COOH/Ny6,10 blend melt mixed at 290 °C for (a) 10, (b) 15, and (c) 30 min. Labels A and B indicate the Ny6,6 and Ny6,10 units, respectively. Labeled peaks correspond to the oligomer species □ (in Figure 4).

together with those pertaining to the homopolymers, and in Table 1 are reported the calorimetric and crystallinity (% C) data. The process of copolymer formation could be monitored also by following the changes in the DSC tracings as a function of the melt-mixing time. Ny6,6-COOH shows a T_g of 48 °C and a T_m of 258 °C (ΔH_m = 61.5 J/g), whereas for Ny6,10 the T_g is 70 °C and T_m is 221 °C (ΔH_m = 61.8 J/g). Both polyamide samples show a low crystallinity: 30−31%, assuming the heats of fusion of the completely crystalline Ny6,6 and Ny6,10 samples are 200.35 and 205.75 J/g, respectively.[31] The crystallinity of all the Ny6,6/Ny6,10 blends in Table 1 were calculated using an average value (203.25 J/g) of the enthalpy of fusion of totally crystalline Ny6,6 and Ny6,10 samples, applied to the procedure reported in the literature.[35,36] The equimolar physical blend (Figure 7) shows two T_g transitions that get closer with the heating time and finally merge to a single T_g transition at 59 °C after 30 min at 290 °C, indicating that a random Ny6,6/Ny6,10 copolyamide was formed.[9] This value is very close to that calculated (58 °C) using empirical Fox equation: $1/T_g = W_1/T_{g1} + W_2/T_{g2}$, where W_1 (45%) and W_2 (55%) are the weight fractions of Ny6,6-COOH and Ny6,10 components, respectively; T_{g1} (48 °C) and T_{g2} (70 °C) are the glass transitions of Ny6,6-COOH and Ny6,10 samples, respectively (see Table 1).

In parts a−j of Figure 8 are reported the DSC traces in the T_m region. The two T_m peaks are present in the blend with values almost unaltered with respect to the single homopolyamides. When the blend is heated at 290 °C up to 15 min, a progressive decrement of the total

Scheme 2



Scheme 3

ΔH_m is observed. This behavior implies that the exchange reaction has occurred (Figure 8d−f). At higher blending times (30 min; Figure 8f and 60 min; Figure 8i, respectively), the DSC traces during first heating run show a single T_m at 193−196 °C (Table 1). This behavior is in agreement with the MALDI data reported above, which clearly indicate that the exchange reaction has occurred and that a random copolymer has been formed.

Data in Table 1 show also that ΔH_m values obtained in the first heating runs for the melt-mixing materials obtained at 5, 30, 60, and 180 min of heating are essentially unchanged with respect to those for the physical blend. An explanation of this result could be that the two repeat units of the copolyamide formed are able to cocrystallize and to accommodate themselves in the same crystal structure.[36,37] However, the DSC traces (Figure 8, parts h and j, respectively), taken after annealing, during the second heating runs, show two T_m peaks at 186−192 °C and at 204−207 °C, respectively, and the % C is strongly reduced in this case (Figure 8, parts h and j; Table 2). These T_m temperatures are both about 30 °C below those of the respective homopolymers ones. This might indicate a different rate of crystallization of short sequences in the copolymer, allowing the formation of two crystalline domains where one of the components predominates with respect to the other,[38] or it might indicate the formation of thin lamellae of Ny6,6/Ny6,10 copolyamides with a different composition of Ny6,6 and Ny6,10 units.

The MALDI spectrum of the annealed Ny6,6/Ny6,10 sample did not change after the DSC second heating run, implying that the copolymer composition and sequence remain unchanged. The annealing process results in a strong reduction of the % C (Table 1) and is probably connected to a similar reduction of the mechanical properties of the annealed Ny6,6/Ny6,10 copolymer.

The crystallinity of the Ny6,6-COOH/Ny6,10 melt-mixed blends were measured also by WAXS analysis. The powder X-ray tracings of the melt reacted blends are very similar to the untreated homopolymers All samples in Table 1 show two well-defined and very similar crystalline diffraction peaks. The first diffraction peak is at about 20.7° (2θ) for all samples while the second peak is at 24.7° (2θ), 24.4° (2θ), and 24° (2θ) for Ny6,6-COOH, Ny6,10, and all Ny6,6COOH/Ny6,10

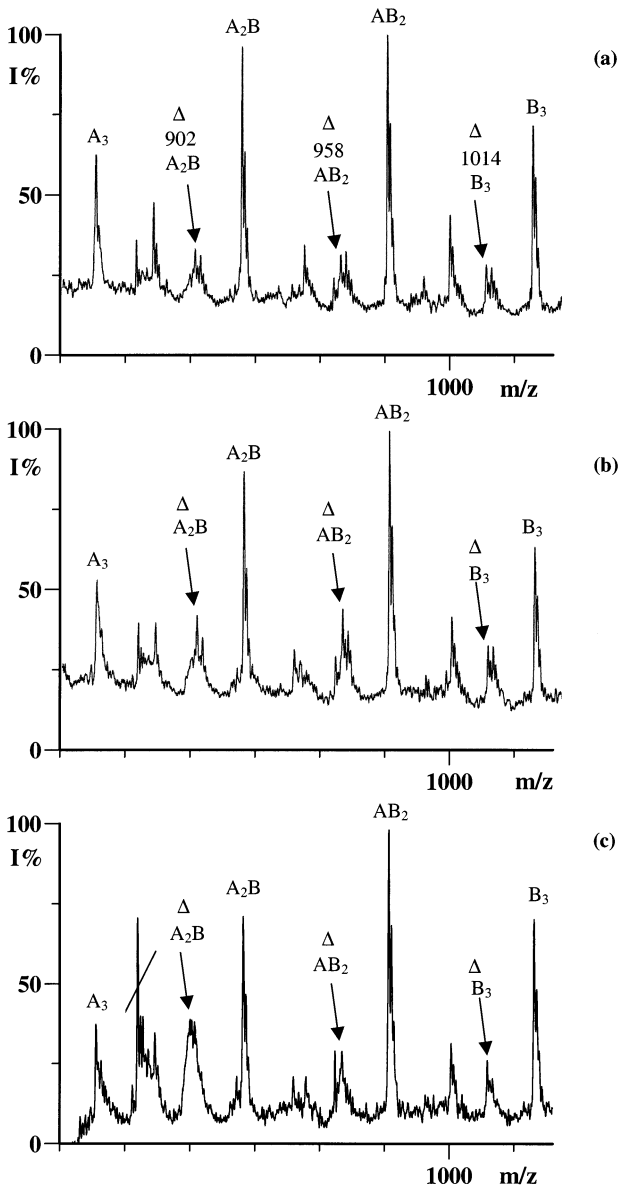


Figure 6. Enlarged section of the MALDI−TOF mass spectra of Ny6,6/Ny6,10 reacted at 290 °C for (a) 30, (b) 60, and (c) 180 min. Labels A and B indicate the Ny6,6 and Ny6,10 units, respectively. Peaks labeled with the symbol Δ indicate copolymer chains terminated with cyclopentanone units.

blends, respectively. Only an increasing contribute of the amorphous halo in the diffraction spectra of the blends obtained at melt-mixing times higher than 15 min was observed.

Conclusions

The results obtained in the present work can be reconciled within the overall scheme of exchange reaction occurring through active chain ends. In fact, the composition of the copolyamides formed by the exchange of Ny66-COOH/Ny6,10 mixtures showed a higher amount of Ny6,6 units, with respect to the initial blends composition, and a higher value of the Ny6,6 average block length, at the beginning of the reaction (10 min). The composition of the copolyamides was found to be equal to the feed composition (50/50), after 30 min of heating, with a random distribution of sequences. The composition and the sequence distributions of the copolyamides remained unaffected even at higher heating

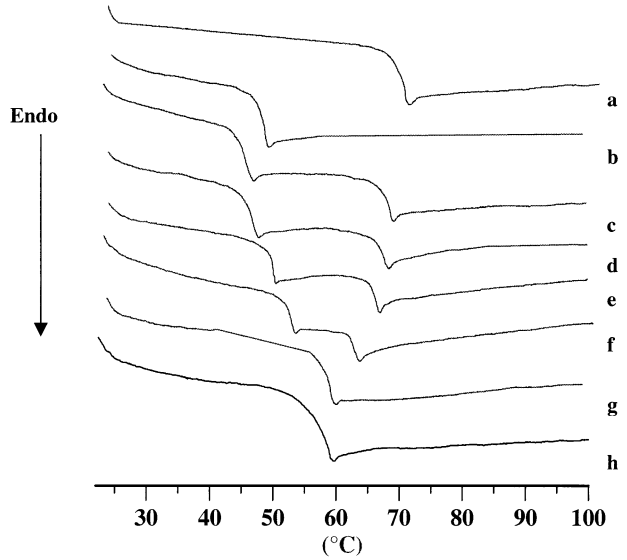


Figure 7. DSC curves in the range 25−100 °C (recorded at 5 °C/min in heating mode) of (a) Ny6,10 and (b) Ny6,6COOH and Ny6,6COOH/Ny6,10 blends reacted at 290 °C for (c) 0, (d) 5, (e) 10, (f) 15, (g) 30, and (h) 60 min.

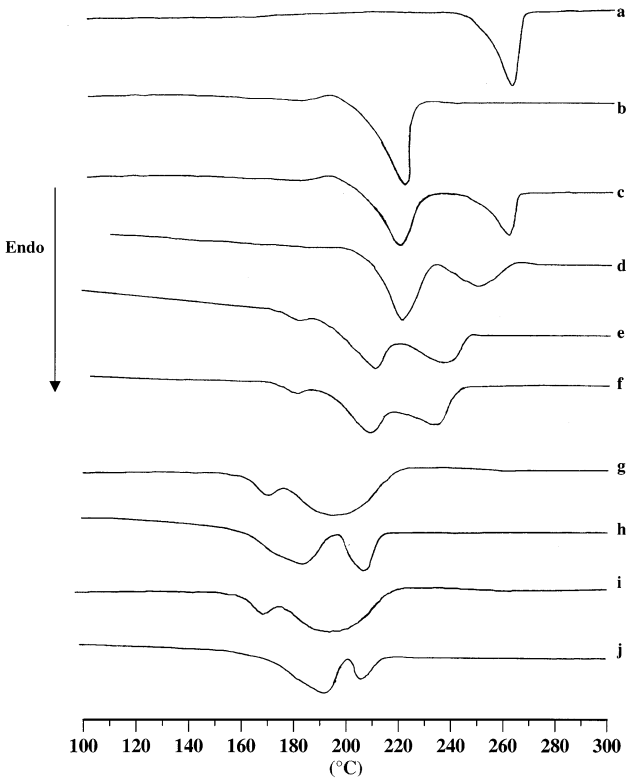


Figure 8. DSC curves in the range 100−300 °C (recorded at 10 °C/min in heating mode) of (a) Ny6,6-COOH and (b) Ny6,10 and Ny6,6-COOH/Ny6,10 blends reacted at 290 °C for (c) 0, (d) 5, (e) 10, (f) 15, (g) 30, (h) 30 (2° heating run), (i) 60, and (j) 60 min (2° heating run).

time (180 min) although some degradation reactions also occurred. Instead, the exchange reaction of a mixture of high molar mass Ny6,6 and Ny6,10 both containing a very low amount of carboxylic chain ends produced segmented copolyamides even at high heating time (150 min).

Acknowledgment. Partial financial support from the Italian Ministry for Public Education, University

and for Scientific and Technological Research (MIUR), and from the National Council of Research (CNR, Rome) is gratefully acknowledged.

References and Notes

(1) Montaudo, G.; Puglisi, C.; Samperi, F. In *Transreactions in Condensation Polymers*; Fakirov, S., Ed.; Wiley-VCH: New York, Chapter 4, p 159, and references therein.
(2) Montaudo, G.; Puglisi, C.; Samperi, F. *Macromolecules* **1998**, *31*, 650−661.
(3) Montaudo, G.; Puglisi, C.; Samperi, F. *J. Polym. Sci., Polym. Chem. Ed.* **1994**, *32*, 15−31.
(4) Montaudo, G.; Montaudo, M. S.; Scamporrino, E.; Vitalini, D. *Macromolecules* **1992**, *25*, 5099−5107.
(5) Pilati, F.; Fiorini, M.; Berti, C. In *Transreactions in Condensation Polymers*; Fakirov, S., Ed.; Wiley-VCH: New York, Chapter 2, p 79, and references therein.
(6) Devaux, J. In *Transreactions in Condensation Polymers*; Fakirov, S., Ed.; Wiley-VCH: New York, Chapter 3, p 125, and references therein.
(7) Xanthos, M.; Warth, H. In *Transreactions in Condensation Polymers*; Fakirov, S., Ed.; Wiley-VCH: New York, Chapter 10, p 411, and references therein.
(8) (a) Takeda, Y.; Paul, D. R. *Polymer* **1991**, *32*, 2771−2777. (b) Takeda, Y.; Paul, D. R. *Polymer* **1992**, *33*, 3899−3907.
(9) Zilberman, M.; Siegmann, A.; Narkis, M. *Polymer* **1995**, *36*, 5065−5067.
(10) Zimmerman, J.; Pearce, E. M.; Miller, I. K.; Muzzio, J. A.; Epstein, I. G.; Hosegood, E. A. *J. App. Polym. Sci.* **1973**, *17*, 849−861.
(11) Khanna, Y. P.; Turi, E. A.; Aharoni, S. M.; Largman, T. U.S. Patent 4,417,032, 1983.
(12) Aharoni, S. M.; Largman, T. U.S. Patent 4,861,667,1983.
(13) Khanna, Y. P. *U.S. Patent* 1989, 4,861,838. Miller, I. K. *J. Polym. Sci., Polym. Chem. Ed.* **1976**, *14*, 1403−1417.
(14) Miller, I. K. *J. Polym. Sci., Polym. Chem. Ed.* **1976**, *14*, 1403−1417.
(15) Kotliar, A. M. *J. Polym. Sci., Macromol. Rev.* **1981**, *16*, 367−395.
(16) Eersel, K. L. L.; Groeninckx, G. *Polymer* **1996**, *37*, 983−989.
(17) (a) Aerdts, A. M.; Eersel, K. L. L.; Groeninckx, G. *Macromolecules* **1996**, *29*, 1041−1045. (b) Eersel, K. L. L.; Aerdts, A. M.; Groeninckx, G. *Macromolecules* **1996**, *29*, 1046−1050. (c) Eersel, K. L. L.; Groeninckx, G.; Mengerink, Y.; Van der Wal, Sj. *Macromolecules* **1996**, *29*, 6744−6749.
(18) Puglisi, C.; Samperi, F.; Di Giorgi, S.; Montaudo, G. Manuscript in preparation.
(19) Kricheldorf, H. R.; Leppert, E.; Schilling, G. *Makromol. Chem.* **1975**, *176*, 81.
(20) Schilling, G.; Kricheldorf, H. R. *Makromol. Chem.* **1975**, *176*, 3341.
(21) Kricheldorf, H. R.; Muehlhaupt, R. *Angew. Makromol. Chem.* **1977**, *65*, 185−192.
(22) Kricheldorf, H. R.; Hull, W. E. *J. Macromol. Sci., Chem.* **1977**, *A11*, 2281−2292.
(23) Kricheldorf, H. R. *Pure Appl. Chem.* **1982**, *54*, 467.
(24) Tran, N.-M.; Djodeyre, E.; Carrière, F. J.; Sekiguchi, H. *Makromol. Chem., Rapid Commun.* **1980**, *1*, 507−512.
(25) Montaudo, M. S.; Montaudo, G. *Macromolecules* **1992**, *25*, 4264−4280.
(26) Montaudo, M. S.; Puglisi, C.; Samperi, F.; Montaudo, G. *Macromolecules* **1998**, *31*, 8666−8676.
(27) Montaudo, G.; Montaudo, M. S.; Samperi, F. In *Mass Spectrometry of Polymers*; Montaudo, G., Lattimer, R. P., Eds.; CRC Press LLC, Boca Raton, FL, 2001, Chapter 10, p 419.
(28) Montaudo, G.; Montaudo, M. S. In *Mass Spectrometry of Polymers*; Montaudo, G., Lattimer, R. P., Eds.; CRC Press LLC, Boca Raton, FL, 2001, Chapter 2 p 41.
(29) Rossback, V.; Niessen, D.; Zahn, H. *Angew. Makromol. Chem.* **1975**, *42*, 1.
(30) Patzold, W. *Polym. Lett.* **1963**, *1*, 269.
(31) Bandrup, J.; Immergut, E. H. *Polymer Handbook*, 3rd ed; John Wiley & Sons: New York, 1989.
(32) Puglisi, C.; Samperi, F.; Di Giorgi, S.; Montaudo, G. *Polym. Deg. Stab.* **2002**, *78*, 369−378.
(33) Ballistreri, A.; Garozzo, D.; Giuffrida, M.; Montaudo, G. *Macromolecules* **1987**, *20*, 2991−2997.
(34) Ballistreri, A.; Garozzo, D.; Giuffrida, M.; Impallomeni, G.; Montaudo, G. *Polym. Deg. Stab.* **1988**, *23*, 25−41.
(35) Kong, Y.; Hay, J. N. *Polymer* **2002**, *43*, 3873−3878.
(36) Gyu Jeong, Y.; Ho Jo, W.; Cheol Lee, S. *Macromolecules* **2000**, *33*, 9705−9711.
(37) Park, J. W.; Kim, D. K.; Im, S. S. *Polym. Int.* **2002**, *51*, 239−244.
(38) Hanna, S.; Windle, A. H. *Polymer* **1988**, *29*, 207−223.

MA021348C