Essential Role of Chain Ends in the Ny6/PBT Exchange. A Combined NMR and MALDI Approach

Filippo Samperi,* Maurizio Montaudo, and Concetto Puglisi

Istituto di Chimica e Tecnologia dei Polimeri, Consiglio Nazionale delle Ricerche, Viale A. Doria, 6−95125 Catania, Italy

Rossana Alicata and Giorgio Montaudo*

Dipartimento di Scienze Chimiche, Universita' di Catania, Viale A. Doria, 6, 95125 Catania, Italy

Received May 12, 2003; Revised Manuscript Received July 31, 2003

ABSTRACT: A combination of NMR and MALDI was found to be a suitable tool to study the exchange reactions that occur during the melt mixing of Nylon-6 and poly(butylene terephthalate) (Ny6/PBT) blends. The results reveal the essential role of carboxyl end groups in the exchange reaction, and allow drawing a detailed mechanism for this reaction. Using Ny6 and PBT samples bearing specific reactive end groups, it was demonstrated that only the carboxyl end groups of PBT and of Ny6 are able to react in the initially biphasic Ny6/PBT blends, so that an outer−inner exchange takes place (Scheme 3). The composition of the copoly(esteramide) obtained at 260 °C in the exchange of Ny6/PBT shows a higher amount of Ny6 units with respect to the initial blend composition and a high value of the Ny6 average sequence length. However, the composition of the copoly(esteramide) obtained at 280 °C was instead found to be equal to the feed composition (50/50), with a random distribution of average sequence lengths. The results obtained in the present work can be reconciled within the overall model of exchange reaction occurring through active chain ends.

Introduction

Blends of condensation polymers such as polyesters and polyamides and in general of polymers bearing reactive functional groups may yield reactions of chemical exchange when they are mixed in the molten state, leading to the formation of block, segmented, or random copolymers.[1−24]

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.

Traditionally, instead, workers have addressed the issue of reactive blending considering mainly the inner functional groups of the homopolymers repeat units, often forgetting about the role of reactive end groups.[1−24]

Failure to realize the importance of polymer terminal units has been commonplace in many reactive blending studies, and the role of reactive chain end groups has remained somehow obscure. As a consequence, the overall picture of exchange reactions taking place in the reactive blending of materials such as polyesters or polyamides has often eluded the research efforts.

In the past few years, we have investigated exchange reactions occurring in the melt-mixing processes of several condensation polymer blends using both end-capped polymer samples and polymers possessing reactive chain end groups, and have formulated a chemical model for these reactive systems.[1−4]

Our model allows making predictions and designing strategies to control the reactions taking place during the melt-mixing process. A major finding is that is possible to distinguish between different mechanisms of exchange by monitoring the composition of the copolymers formed in the melt-mixing process.[1−4] More specifically, the exchange reaction may proceed by the following methods: (i) direct exchange between two functional groups located inside the polymer chains (referred to inner−inner exchange); (ii) attack of reactive chain ends on inner groups (referred to inner−outer exchange).[1−4]

If an inner−inner exchange reaction occurs, the molar composition of the resulting copolymer is predicted to be constant and equal to the feed ratio of the two homopolymers, independent of the extent of reaction and the initial molar mass of the reactants.[1−4]

Alternatively, if an outer−inner exchange reaction takes place, the composition and structure of the copolymer formed is predicted to vary with the extent of reaction, depending both on the reactivity and the concentration of chain ends.[1−4]

Nylon-6 (Ny6) and poly(butylene terephthalate) (PBT) lead to incompatible blends in the melt,[5] and several workers have investigated several aspects related to the processing, compatibilization, morphology, and mechanical properties of these blends.[5−11] However, little attention has been paid to the role of chain ends in this exchange reaction.

To investigate this aspect, a model *alt*-copoly(esteramide) and several Ny6 and PBT samples containing appropriate end groups (Table 1) have been synthesized for this study. A combined NMR and MALDI−MS analysis of the reaction products has allowed the identification of the structural details of the copolymers produced in the exchange, and a detailed reaction scheme has been deduced from the data collected.

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 dyad sequences.[12−17]

The sequence and composition analysis in copolymers having large comonomer subunits, can be often achieved

* Corresponding author.

10.1021/ma0346153 CCC: $25.00
Published on Web 08/29/2003

Table 1. η_{inh}, Molar Mass Data, Amounts of Amino and Carboxyl End Groups, and DSC Measurements for Ny6 and PBT Samples and for an *alt*-Copoly(esteramide)

sample	η_{inh} (dL/g)	M_v	[NH_2] (mmol/Kg)	[OH] (mmol/Kg)	[COOH] (mmol/Kg)	T_g (°C)	T_m (°C)
Ny6	0.70	30 300[a]	36		10	59	219
Ny6−NH_2	0.30	9950[a]	82.73		40	58	217
Ny6−COOH	0.21	5900[a]	2.51		160		211
PBT	0.98	29 000[b]		18	45	72	223
PBT−OH	0.122	2300[b]		330[c]	30		204
PBT−COOH	0.21	4400[b]			190	92	199
alt-copolyesteramide (CL−B−CL−T)	0.17		52	35	86		175

[a] Determined by viscosity method using the Mark−Houwink equation: $[\eta] = KM_v^a$ with $K = 30.3 \times 10^{-3}$ mL/g and $a = 0.75$ [b] Determined by viscosity method using the Mark−Houwink equation: $[\eta] = KM_v^a$ with $K = 21.5 \times 10^{-3}$ mL/g and $a = 0.82$ [c] A similar value (310 mmol/kg) was calculated from the ^{1}H NMR spectrum.

by mass spectrometry (MS),[18−21] which is complementary to NMR analysis.

In the past decade, the MS analysis of polymers has taken advantage from the development of matrix-assisted laser desorption ionization (MALDI) time-of-flight MS, a soft ionization technique that possesses high sensitivity and allows the detection of intact polymer molecules and their identification as mass resolved polymer chains.[20−21]

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,[18] providing a new method for deducing the sequence distributions and composition of comonomers in copolymers by MS techniques.[18−21]

The MS method has been successfully applied also to the characterization of the copolymers obtained in the processing of several reactive blends.[1−4]

Experimental Section

Materials. High molar mass (MM) PBT and Ny6 polymer samples were supplied by Aldrich Chemical Co. and were ground from pellets to fine powder in the presence of solid CO_2. They were purified from the lower MM oligomers by appropriate solvent/nonsolvent solution/precipitation method and successively dried at 60 °C in a vacuum oven for 1 week before use. Some characteristics of these polymers are listed in Table 1, whereas in Table 1S are reported their ^{1}H and ^{13}C NMR resonance signals.

All solvents and reagents used were purchased from Aldrich Chemical Co. (Italy), with the exception of deuterated solvents that were supplied by Merck.

The reagents used for the syntheses were appropriately purified before use. Benzoic acid was purified by crystallization from water; 1,4-butanediol was purified by vacuum distillation and stored on molecular sieves; terephthaloyl dichloride (supplied by Sigma-Aldrich Chemical Co.) was crystallized from *n*-hexane. Terephthalic acid (TA), 1,6-hexamethylenediamine (HMDA), decylamine, *N*,*N*-dimethylaniline, ϵ-aminocaproic acid, diphenylsulfone (DPSO), *p*-toluenesulfonic acid monohydrate (*p*-TSOH·H_2O), and the MALDI matrix 2-(4-hydroxyphenylazo)benzoic acid (HABA) were used as supplied.

Reactive Blending Procedure. All Ny6/PBT blends were melt mixed in a glass reactor, under stirring and nitrogen flow, at a temperature between 260 and 280 °C for 1 h, using an equimolar mixture in monomer units of Ny6 and PBT samples (corresponding to 33/64 Ny6/PBT weight/weight ratio). Ny6/PBT−COOH blends were also reacted at 280 °C for 30, 60, and 120 min.

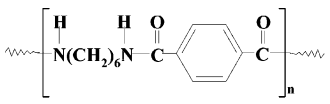
^{1}H NMR analysis showed that all the melt-mixed blends have a molar composition close to that of the starting mixtures (50:50 mol/mol).

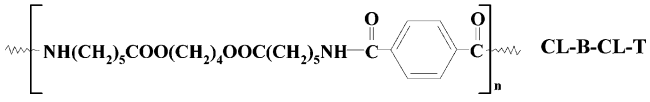
Synthesis of Functionalized Ny6 and PBT. The characterization of Ny6 and PBT samples bearing specific end groups is reported in Table 1. The Ny6−COOH sample was obtained by acidolysis of high molar mass Ny6 (M_w = 45 000) with benzoic acid, using a molar ratio 1/0.2, at 240 °C in DPSO in inert atmosphere (N_2). Ny6-NH_2 polymer was obtained by partial aminolysis of high molar mass Ny6 with decylamine, in a molar ratio 1/0.2, at 240 °C, under nitrogen flow, in the presence of DPSO.

The PBT−OH sample was obtained by melt-polymerization of terephthaloyl dichloride with and 1,4-butanediol, (34.46 mmol) in the molar ratio 1/1.7, at 160 °C for 2 h, under vigorous stirring, then at 200 °C for 1 h, and afterward at 240 °C for 1 h.

The PBT−COOH sample was prepared by a two-step solution−polymerization. In the first step, 49.21 mmol of terephthaloyl dichloride and 46.86 mmol of 1,4-butanediol were reacted at 70 °C for 24 h in the presence of *N*,*N*-dimethylaniline (49.21 mmol) as acid acceptor in TCE as solvent, under N_2 flow. Then, an excess of terephthaloyl dichloride (1/10 mol respect to the initial amount) was added to the mixture, to cap eventually free hydroxyl end groups, and after 1 h, the solvent was removed by vacuum distillation. The solid residue was dissolved in 100 mL of dimethylformamide (DMF) to hydrolyze the acyl chloride end chains (second step) with H_2O (1 mL) at 100 °C for 24 h, in the presence of *N*,*N*-dimethylaniline and under nitrogen flow. The solid polymer was finally recovered by precipitation in a large excess of H_2O (1000 mL). Functionalized Ny6 and PBT samples have been characterized by NMR and MALDI. NMR chemical shifts are reported in Table 1S. The MALDI spectra have been reported elsewhere.[22−23]

Synthesis of Model Polymers. As discussed below, two new sequences are formed when exchange reactions between Ny6 and PBT occur in the molten state. To assign the NMR signals due to caprolactam−terephthalic (CL−T) and caprolactam-butylene (CL−B) sequences, we have synthesized appropriate polymers, such as poly(hexamethylene terephthalamide) (Ny6T) and *alt*-copoly(esteramide) (CL−B−CL−T).

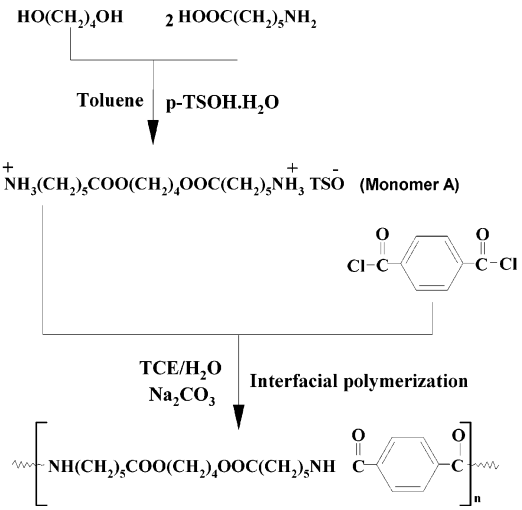




(a) Poly(hexamethylene terephthalamide) (Ny6T). A melt-polymerization, starting from an equimolar ratio of HMDA and TA, was carried out to synthesize the Ny6T sample. First, 5 g (30 mmol) of TA and 3.5 g (30 mmol) of HMDA were placed in a three-necked flask, and the temperature was slowly raised from 180 to 260 °C. The reaction mixture was maintained at this temperature for 20 min under nitrogen flow and then under vacuum for 1 h to allow reaching completion. The polymer obtained was purified by precipitation in water and dried at 60 °C under vacuum. The sample was characterized by DSC, NMR, and MALDI. The NMR signals are assigned in Table 1S.

(b) *alt*-Copoly(esteramide) (CL—B—CL—T). An alternating copoly(esteramide) was synthesized according to Scheme 1.

Scheme 1



Monomer A was synthesized according to the procedure reported in the literature.[24] The white solid, purified by crystallization from ethanol, was characterized by DSC (T_m = 146 °C) and ^{1}H and ^{13}C NMR (the chemical shifts are reported in Table 1S).

Polymerization. A solution of monomer **A** (4.56 mmol) and the proton acceptor (9.116 mmol of Na_2CO_3) in 45 mL of water was rapidly added to 40 mL of a solution of terephthaloyl dichloride (4.56 mmol) in tetrachloroethane, under a rapid stirring in a precooled reactor vessel. After 10 min, the formed polymer and the reaction mixture were precipitated in a large excess of acetone, then repeatedly washed with acetone before drying in a vacuum oven at 60 °C. The copoly(esteramide) was characterized by ^{1}H and ^{13}C NMR using a $CDCl_3$/d-TFA/$(CF_3CO)_2O$ mixture as a solvent. The pertinent assignments are reported in Table 1S.

NMR Analysis. The ^{1}H and ^{13}C NMR analyses were performed using a Bruker A-CF200 spectrometer at room temperature, using deuterated solvent and tetramethylsilane (TMS) as internal standard. A mixture of $CDCl_3$/$(CF_3CO)_2O$/CF_3COOD (70:17:13 v/v) was used to analyze the Ny6 samples and all PBT/Ny6 blends, while the PBT−OH sample was analyzed in deuterated 1,1,2,2-tetrachloroethane (TCE-d_2).

The ^{13}C NMR 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 μs and delay of 1 s were used for about 20 000 accumulations.

Selected ^{1}H and ^{13}C NMR spectra were also recorded at 500 MHz, using a ^{UNITY}INOVA Varian NMR spectrometer. No sensible advantage was however observed at this higher resolution.

NMR Calculations. The molar fractions of dyads and triads, average sequence lengths, and degrees of randomness in the Ny6/PBT copolymers obtained by melt mixing were calculated from the ^{13}C NMR data using the method of Devaux et al.[12]

MALDI—TOF Mass Spectrometry. MALDI−TOF mass spectra were recorded both in linear mode and in reflectron mode, using a Voyager-DE STR (Perseptive Biosystem) mass spectrometer instrument, equipped with a nitrogen laser emitting at 337 nm, with a 3 ns pulse width, and working in positive ion mode. The accelerating voltage was 20−25 kV, and the grid voltage and delay time (delayed extraction, time lag), were optimized for each sample to achieve the higher mass resolution, expressed as the molar mass of a given ion divided by the full width at half-maximum (fwhm). The laser irradiance was maintained slightly above the threshold.

2-(4-Hydroxylphenylazo)benzoic acid (HABA) 0.1 M in trifluoroethanol (TFE) or in hexafluoro-2-propanol (HFIP) solvent, was used as matrix.

The concentration of all Ny6 samples was 1−2 mg/mL in TFE and 2−3 mg/mL in HFIP for PBT samples. The PBT/Ny6 blends studied were dissolved in HFIP to obtain a concentration of about 2 mg/mL. Appropriate volumes of polymer solution and matrix solution were mixed in order to obtain a 1:1, 1:2, and 1:3 v/v ratio. A 1 μL aliquot of each sample/matrix mixture was spotted on the MALDI sample holder and slowly dried to allow matrix crystallization.

MACO4 Calculation. MALDI−TOF MS data were analyzed by using the MACO4 program.[18] MACO4 accepts as input the following: (a) the experimental mass spectrum; (b) the mathematical model that defines the distribution of comonomers along the chain, information about the type of process by which the oligomers subjected to MS were obtained. 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 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[18] (AF): $AF = q\Sigma_i(I_i^{expt} - I_i^{calcd})^2$; where I_i^{expt} 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/PBT copolyamide prepared by melt mixing of the corresponding homopolymers can be obtained.

Viscometry. The inherent viscosities ($\eta_{inh} = \ln(\eta_{rel}/C)$), were measured using an Ubbelohde viscometer, at a concentration of 0.5 mg/dL of Ny6 or PBT sample in trifluoroethanol (TFE) and phenol/tetrachloroethane 60/40 w/w, respectively, at 30.0 ± 0.1 °C.

DSC Measurements. The thermal behavior of all polymer samples was investigated in N_2 atmosphere by a Mettler differential scanning calorimeter (DSC 20), using a heating rate of 10 °C/min, between 30 °C and the desired upper temperature limit.

The T_g values were computed by the midpoint method; the melting point temperatures (T_m) weretaken as the maximum of the endothermic peak.

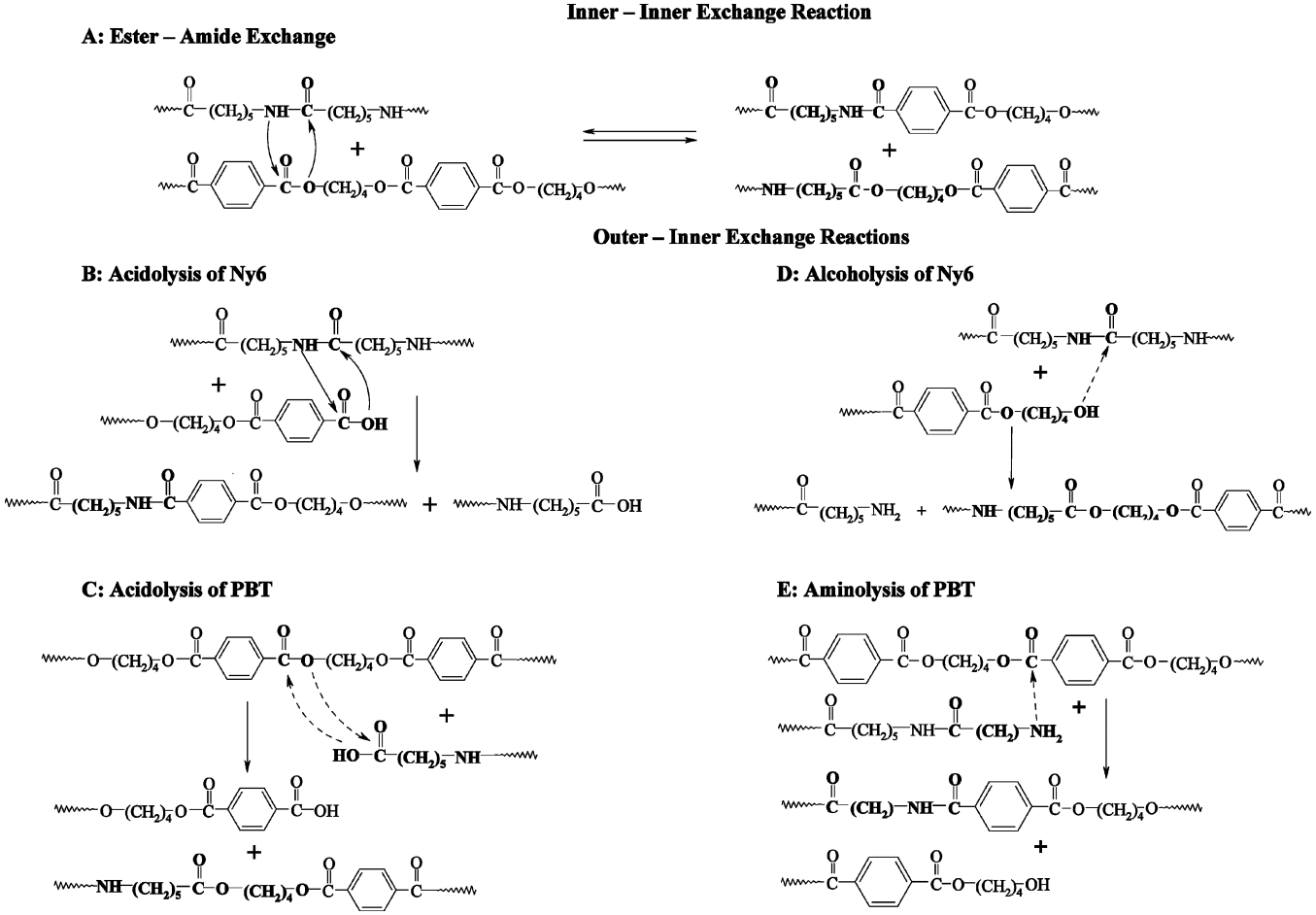
In Table 1 are reported the specific values of T_g and T_m for all polymer samples used in this work.

End Groups Determination. In Table 1 are reported the amounts of end groups for the Ny6 and PBT samples used in this work. The amine and carboxyl chain end concentrations for Ny6 samples were measured by the procedure described in the literature,[25,26] and specific values are reported in Table 1. The concentration of carboxyl end groups in the PBT samples was determined by titration method used by Jabarin et al.[27] The amount of hydroxyl end groups in the PBT samples was determined by FT-IR and confirmed by ^{1}H NMR analysis in $C_2D_2Cl_4$ at 60 °C.

Results and Discussion

Ny6 and PBT are not compatible in the molten state, and their blends are biphasic, presenting therefore a reduced contact surface.[5−11] However, when the exchange takes place, the initial homopolymers are progressively converted into the new copoly(esteramide) chains, which act as partial compatilizers for the Ny6/PBT blend, thus enhancing the rate of the exchange reaction. The exchange reactions which might occur in the melt mixing of Ny6/PBT blends are summarized in Scheme 2.

Scheme 2. Exchange Reactions That Might Occur during Thermal Treatment of Ny6/PBT Blends



The inspection of the DSC traces in Figure 1 shows that the formation of a copolymer is clearly observable when a high molar mass Ny6 sample is melt mixed at 280 °C for 1 h with a sample of PBT carboxyl-terminated (PBT−COOH). In parts a−c of Figure 1 are shown the DSC traces corresponding to Ny6, to PBT, and to their physical mixture, respectively. The trace in Figure 1d shows that the exchange reaction has taken place, since the strong endothermic peaks corresponding to the melting points of the two homopolymers have disappeared in the blend cured at 280 °C for 1 h, and also because contrary to the physical blend (Figure 1c) showed only one glass transition (T_g) at 69 °C, indicating that a random Ny6/PBT copoly(esteramide) was formed. This value is close to that calculated (76 °C) using the empirical Fox equation: $1/T_g = W_1/T_{g_1} + W_2/T_{g_2}$, where W_1 (37%) and W_2 (63%) are the weight fractions of Ny6 and PBT−COOH components, respectively; T_{g_1} (59 °C) and T_{g_2} (92 °C) are the glass transitions of Ny6 and PBT−COOH samples, respectively (see Table 1).

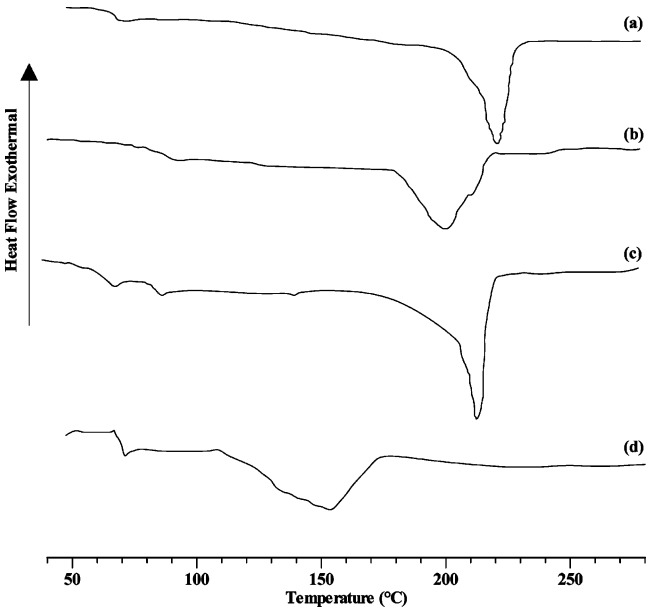


Figure 1. DSC (second scans at 10 °C/min in heating mode) of (a) Ny6, (b) PBT−COOH, (c) Ny6/PBT−COOH physical blend, and (d) Ny6/PBT−COOH blend melt mixed at 280 °C for 1 h.

As discussed in detail below, the copoly(esteramide) formation was found to occur only to a negligible extent when a PBT sample without carboxyl end groups was used in the melt-mixing process with Ny6, implying that the exchange reaction does not proceed through an inner−inner process (Scheme 2, reaction A). An outer−inner reaction appears therefore responsible for the exchange. Several reactions of this kind are possible, and those potentially involved in the melt blending of Ny6 and PBT are summarized in Scheme 2, reactions B−E.

We have ascertained that the ester−amide exchange (reaction A, Scheme 2) occurs only to a minor extent up to 290 °C, as demonstrated by the following experiments. Equimolar mixtures of high molar mass PBT and Ny6, both containing a negligible amount of reactive chain ends (Table 1), were melt mixed in the temperature range 270−290 °C for 1 h. From the inspection of

the ^{13}C NMR spectrum reported in Figure 1Sa, it is concluded that the spectrum of the blend processed at 270°C for 1 h is identical to that of the physical blend, indicating that exchange reactions do not occur at this temperature. Instead, in the ^{13}C NMR spectrum of the PBT/Ny6 blend heated at 290 °C for 1 h (Figure 1Sb), several new signals with low intensity appear, which belong to copoly(esteramide) sequences (see below). This suggests that at 290 °C only a limited exchange takes place when high molar mass PBT and Ny6 are mixed. Similar results were obtained when Ny6/PBT blends were melted in the presence of 0.5−1 wt % of one of the alleged catalysts for this exchange (such as $Ti(OBu)_4$, $SnBu_2O$, and $ZnAc_2/Sb_2O_3$), as reported in the literature,[28] indicating that these compounds actually do not possess catalytic activity with respect to inducing a Ny6/PBT exchange.

No further reaction was observed when these blends were melt mixed in the presence of DPSO (30%w). The latter compound is inert, and it is used to lower the viscosity of the melt and to increase the miscibility of PBT and Ny6 in the molten state.

We believe that even the limited exchange reaction observed (Figure 1Sb) is not due to an inner ester−amide exchange (reaction A, Scheme 2). In fact, it has been recently shown that the onset of the PBT thermal decomposition is at about 280 °C and that this process leads to the formation of carboxyl-terminated PBT.[29] It is therefore conceivable that the copoly(esteramide) originates from the reactive PBT carboxyl ends formed by thermal degradation of PBT at 290 °C.

To find out which end groups are capable of inducing the Ny6/PBT exchange, we have performed a series of melt-mixing experiments using polymer samples having selected chain ends (Table 1). The results obtained show that the following exchange reactions do not occur to a sizable extent: (i) the alcoholysis of Ny6 operated by alcoholic end groups of PBT (reaction D, Scheme 2); (ii) the acidolysis of PBT operated by carboxylic end groups of Ny6 (reaction C, Scheme 2); (iii) the aminolysis of PBT operated by amino end groups of Ny6 (reaction E, Scheme 2). Instead, the acidolysis of Ny6 operated by carboxylic end groups of PBT (reaction B, Scheme 2) was found to take place, and this exchange reaction went to completion when blends of high mass Ny6 with PBT−COOH (Table 1) were heated at 280 °C.

This result is nicely shown by the ^{13}C NMR spectra in Figure 2. In Figure 2a is reported the ^{13}C NMR spectrum of the physical blend Ny6/PBT−COOH, whereas in Figure 2b is shown that of the blend heated at 280 °C for 1 h. The latter spectrum shows other signals corresponding to the copoly(esteramide) formed during the melt mixing. These signals are identical to those observed in the spectrum in Figure 1Sb, and have been assigned in Tables 2 and 1S. The ^{13}C NMR assignments are supported by the spectrum shown in Figure 2c, corresponding to an authentic sample of the alternating copoly(esteramide) synthesized for this purpose (see Experimental Section and Tables 2 and 1S). The assignments of the signals present in the NMR (^1H and ^{13}C) spectra of the Ny6/PBT melt-mixed blends were carried out according to those of the polymer models reported in Table 1S. The necessity of relying on the assignments of the alternating copoly(esteramide), descends from the observation that a generic "random Ny6/PBT copoly(esteramide)" might be missing the caprolactam-butylene sequence (CL−B). In fact, the peak appearing at 65.7 ppm in the ^{13}C NMR spectrum of the copoly(esteramide) (Figure 1Sb), is matched by a similar peak appearing in Figure 2c, which can be firmly assigned to the CL−B sequence on the basis of the ^{13}C NMR signals reported in Table 2 (see also the assignments for the compound model A in Table 1S). The presence of these CL−B sequences in the copolymer is diagnostic for a specific exchange reaction (Scheme 3, route 3), thus allowing us to establish the mechanism of the overall process.

The above data indicate that the carboxyl ends of PBT are able to attack the amide groups along the Ny6 chains, thus cutting (statistically) the Ny6 molecules in two pieces and yielding a copoly(esteramide) molecule plus a shorter Ny6 homopolymer chain (Scheme 2B).

However, this conclusion encounters a difficulty. According to Scheme 2B, the reaction should stop when the reactive carboxyl ends of PBT in the PBT−COOH sample have been consumed in the exchange reaction.

Instead, the reaction goes to completion, and no homopolymers are found after 1 h at 280 °C. It is therefore evident that another exchange process comes into place as the reaction progresses.

A plausible pathway for this exchange is given by the observation that each acidolysis reaction of Ny6 (Scheme 2B) generates a aliphatic carboxylic end group on the Ny6 chain (these oligomers were existing only at trace levels initially).

The carboxyl-terminated Ny6 oligomers, are born in-situ within the reacting blend, and might participate in the process by inducing the acidolysis of PBT (Scheme 2C).

Although Ny6 chains with carboxylic end groups are unreactive when mixed with high molar mass PBT (see above), the initially incompatible blend may become partially compatible by effect of the block copoly(esteramide) formed through the attack of the carboxyl ends of PBT. In this homogeneous environment, the carboxylic end groups generated on the Ny6 chain might promote the exchange reaction.

The reaction sequence responsible for the formation of Ny6/PBT copoly(esteramide) in the melt-mixing process of the Ny6/PBT−COOH blend is summarized in Scheme 3.

In Scheme 3, PBT−COOH chains (**I**) react with Ny6 and are consumed in two reactions: in route 1, to yield copoly(esteramide) oligomers (**III**) containing butylene−terephthalate−caprolactam (B−T−CL) sequences, and in route 2, to yield Ny6 chains (**V**) containing terephthalic acid ends.

Route 1 also generates new species, i.e., Ny6 chains with aliphatic carboxyl end groups (**IV**), which are now able to react (route 3, Scheme 3) with copoly(esteramide) oligomers (**III**) to yield copoly(esteramide) oligomers (**VIII**) containing caprolactam−terephthalate−caprolactam (CL−T−CL) sequences.

Route 4 takes into account the ability of Ny6 with terephthalic acid ends (**V**) to react with copoly(esteramide) oligomers (**III**), and to yield copolymer oligomers (**VII**) containing butylene-caprolactam (B−CL) sequences, plus oligomers having PBT−COOH (**I**) type terminal groups.

The latter route closes the loop, and the reactions shown in Scheme 4 describe therefore a cycle allowing the regeneration of the reactive carboxyl ends, up to the consumption of the two initial homopolymers and to the completion of the exchange process in the Ny6/PBT

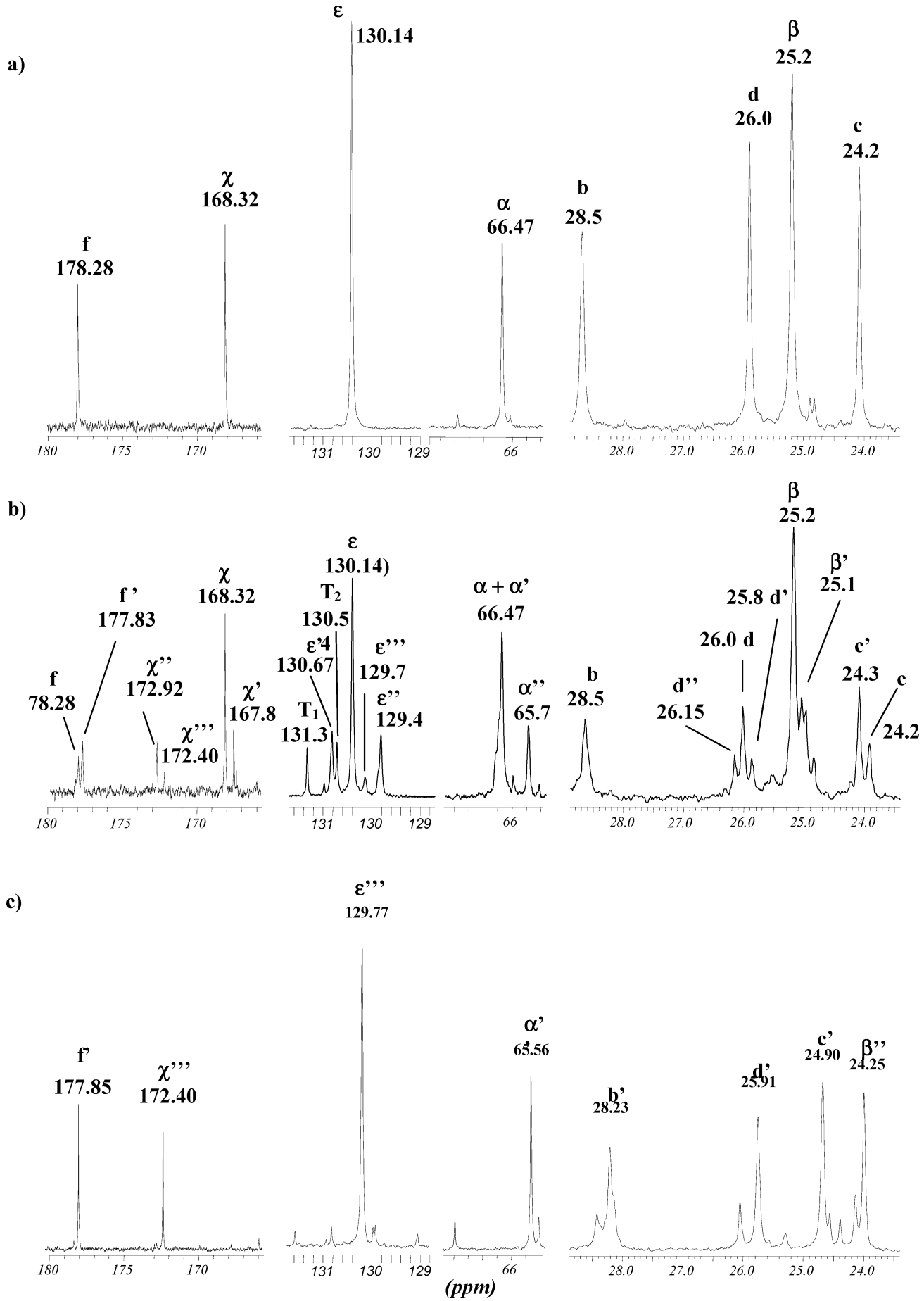
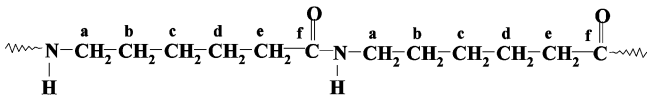
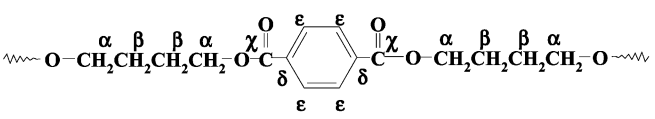
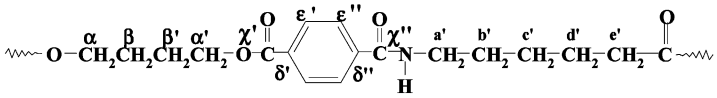
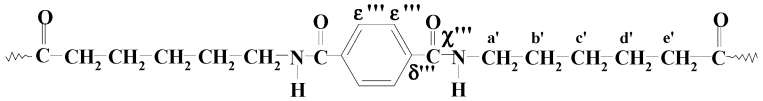
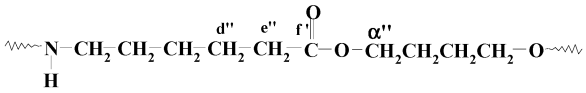


Figure 2. ^{13}C NMR spectra of (a) Ny6/PBT−COOH physical blend, (b) Ny6/PBT−COOH blend heated at 280 °C for 1 h, and (c) *alt*-copoly(esteramide).

Table 2. Carbon Signals Assignments of Dyads and Triads Sequences in the Copolymers Formed during Melt-Mixing of Ny6/PBT Blends, As Observed in Their NMR Spectra

Sequence	Structures		Shift (ppm) Proton	Carbon
CL-CL[a]		a	3.76	44.95
		b	*1.72*	28.71
		c	1.40	24.14
		d	*1.72*	25.94
		e	2.87	38.39
		f	-	178.28
B-T-B[b,c]		α	4.54	66.47
		β	2.07	25.26
		χ	-	168.32
		δ	-	133.94
		ε	8.16	130.14
B-T-CL		a'	3.79	47.60
		b'	1.93	28.25
		c'	--	24.30
		d'	--	26.09
		e'	2.45	34.29
		α	4.54	66.50
		β	2.06	25.24
		α'	3.55	65.79
		β'	--	25.13
		δ'	--	134.19
		δ''	--	136.88
		ε'	8.22	130.67
		ε''	7.84	129.40
		χ'	--	167.81
		χ''	--	172.92
CL-T-CL		a'	3.79	47.60
		b'	1.93	28.25
		c'	--	24.30
		d'	--	26.09
		e'	2.45	34.29
		ε'''	--	129.81
		δ'''	--	135.70
		χ'''	---	172.40
CL-B		d''	--	25.84
		e''	2.65	32.91
		f'	--	177.84
		α''	4.27	63.63

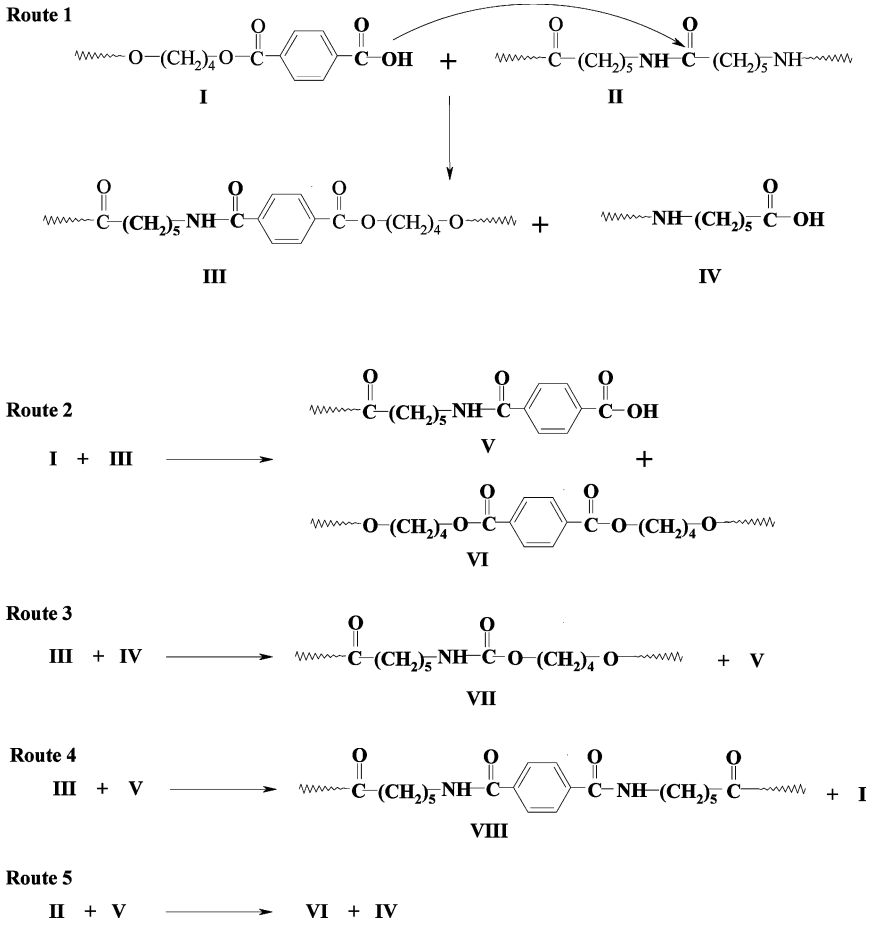
[a] CL = $-NH(CH_2)_5CO-$. [b] B = $-O(CH_2)_4O-$. [c] T = $-OC-Ph-CO-$.

blends. Scheme 3 also predicts that the number of carboxyl end groups is not depleted in the course of the exchange reaction, and therefore can go to completion, producing a random copoly(esteramide) with the same composition of the initial homopolymers mixture. Evidence supporting this complex reaction mechanism comes from the ^{13}C NMR spectra presented in Figures 2, and 1S and in Tables 2 and 1S, using the chemical shift of the polymer models reported in Table 1S. In fact, the spectral assignments in Table 2 indicate the presence of the CL−B, B−T−B, B−T−CL and CL−T−CL sequences in the Ny6/PBT copoly(esteramides) formed. As anticipated above, the CL−B dyad is diagnostic for the occurrence of route 3, Scheme 3, an essential feature of the reaction mechanism proposed.

The ^{13}C NMR spectra yield information on the sequences existing along the copolymer chains, but do not allow detection of the reactive oligomers and the chain ends hypothesized in Scheme 3. This evidence is provided in detail by the MALDI mass spectrometric analysis.

The MALDI spectra of the homopolymers Ny6 and of PBT−COOH have been already reported;[22,23] therefore, only portions of these spectra are shown in Figure 2S. The most intense mass peaks in Figure 2Sa belong to cyclic Ny6 oligomers, whereas linear Ny6 carboxyl-terminated oligomers (Table 3) are also present with lower intensity. PBT oligomers terminated with carboxyl groups are instead the only mass series present in the MALDI spectrum in Figure 2Sb.

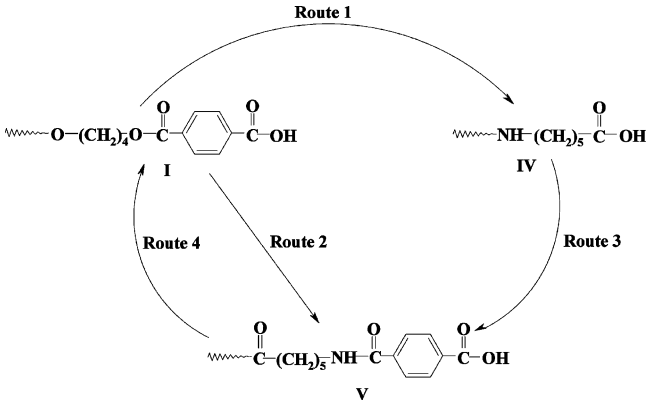
Scheme 3. Sequence of Reactions Responsible for the Formation of Ny6/PBT Copolyesteramide in the Melt-Mixing Process of Ny6 and Carboxyl-Terminated PBT at 280 °C



Ny6/PBT−COOH blends reacted for 1 h at 260, 270, and 280 °C were analyzed by MALDI. Portions of the spectra are reported in Figure 3, and the peaks present are assigned as in Table 3.

The main peaks in the spectrum of the blend melt mixed at 260 °C (Figure 3a) are due to Ny6 cyclic oligomers (peaks $A_{n,0}$) and to the linear Ny6 oligomers with terephthalic acid end groups (peaks, $B_{n,0}$ and $B'_{n,0}$). The peak series C (Figure 3a) is due to the Ny6 oligomers bearing carboxyl chain ends, formed owing to the initial acidolysis exchange (route 1, Scheme 3). Figure 3a shows also peaks corresponding to Ny6-PBT co-oligomers belonging to species $A_{n,m}$ and $B_{n,m}$ (Table 3). Peaks corresponding to Ny6 oligomers bearing terephthalic acid ends ((peaks, $B_{n,0}$ and $B'_{n,0}$, Table 3) are also present in the spectrum of the Ny6/PBT−COOH blends melt mixed at 270 °C (Figure 3b), together with the peaks of the Ny6/PBT co-oligomers ($B_{n,m}$). The inspection of the spectrum in Figure 3b also reveals that the homopolymer Ny6 (peaks $A_{n,0}$) is absent, and therefore it has reacted completely. Finally, the spectrum of the Ny6/PBTCOOH blends reacted at 280°C for 1 h (Figure 3c) shows an increased intensity of the peaks due to Ny6-PBT co-oligomers (species $A_{n,m}$ and $B_{n,m}$), confirming the progress of the exchange reactions. The peaks series C, corresponding to the Ny6 oligomers bearing carboxyl chain ends, has disappeared in Figure 3c, as well as the linear Ny6 oligomers with terephthalic acid end groups (peaks, $B_{n,0}$ and $B'_{n,0}$). Therefore, the MALDI spectrum in Figure 3c shows only peaks due to Ny6/PBT co-oligomers (species $A_{n,m}$ and $B_{n,m}$), implying that the exchange reaction has gone to completion. MALDI spectra of the Ny6/PBT−COOH melt mixed at 280 °C for 30 and 120 min are very similar to that obtained at 60 min (Figure 3c), indicating that the exchange reaction has goes to completion after about 30 min of reaction time at 280 °C.

Scheme 4



In Figure 4, are plotted the intensity/temperature profiles, of the MALDI peaks corresponding to oligomers bearing the most relevant reactive oligomers hypothesized in Scheme 3. The four curves in Figure 4 represent a classic example of consecutive kinetic events and nicely fit the predictions of Schemes 3 and 4. In fact, the intensity of the pristine Ny6 oligomers (labeled as **II** in Figure 4 and in Scheme 3) decreases steadily, as the reaction proceeds. The Ny6 oligomers bearing

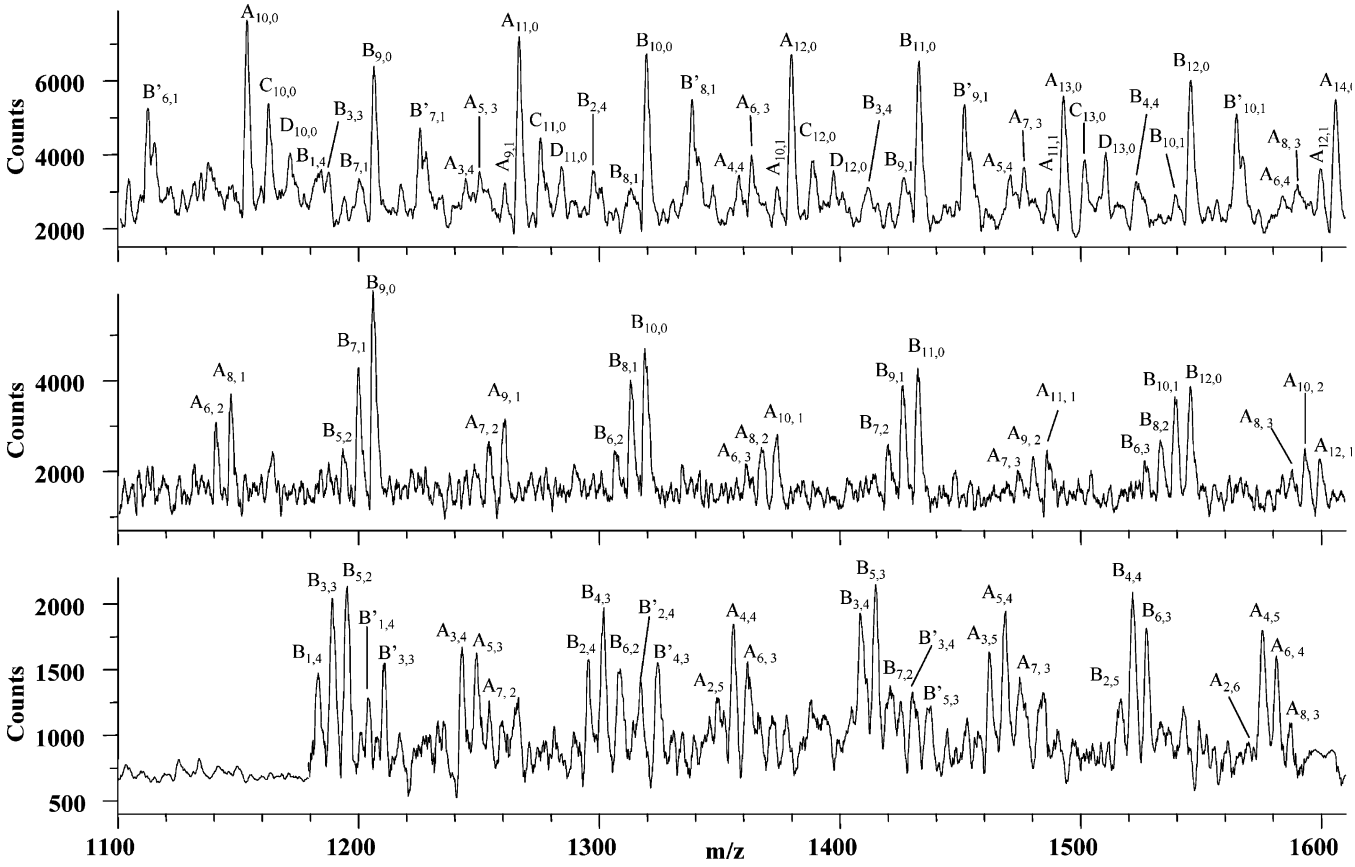
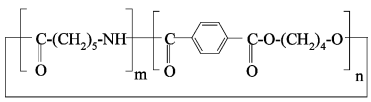
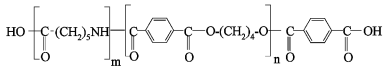
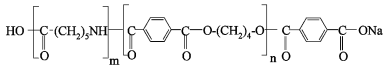
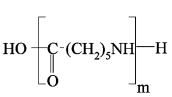


Figure 3. Enlarged section of the MALDI−TOF mass spectra of Ny6/PBTCOOH blend melt mixed for 60 min at (a) 260, (b) 270, and (c) 280 °C.

Table 3. Structural Assignments of Peaks Displayed in the MALDI−TOF Mass Spectra of Melt Mixed Ny6/PBT−COOH Blends Reported in Figure 3

Species	Structures	$[M+Na]^+$ (m,n)
A		1142 (6,2); 1148 (8,1); 1154 (10,0); 1243 (3,4); 1249 (5,3); 1255 (7,2); 1261 (9,1); 1267 (11,0); 1350 (2,5); 1356 (4,4); 1362 (6,3); 1368 (8,2); 1374 (10,1); 1380 (12,0);1463 (3,5); 1469 (5,4); 1475 (7,3); 1481 (9,2); 1487 (11,1); 1493 (13,0);1570 (2,6); 1576 (4,5); 1582 (6,4); 1588 (8,3); 1594 (10,2); 1600 (12,1);1606 (14,1)
B		1184 (1,4); 1189 (3,3); 1195 (5,2); 1201 (7,1); 1207 (9,0); 1296 (2,4); 1302 (4,3); 1308 (6,2); 1314 (8,1); 1320 (10,0); 1409 (3,4); 1415 (5,3); 1421 (7,2); 1427 (9,1); 1433 (11,0); 1516 (2,5); 1522 (4,4); 1528 (6,3); 1534 (8,2); 1540 (10,1); 1546 (12,0)
B'		1206 (1,4); 1212 (3,3); 1218 (5,2); 1318 (2,4); 1324 (4,3); 1330 (6,2); 1431 (3,4); 1437 (5,3); 1443 (7,2); 1538 (2,5); 1544 (4,4); 1550 (6,3);
C		1172 (10); 1285 (11); 1398 (12); 1411 (13)

carboxyl chain ends (labeled as **IV** in Figure 4 and in Scheme 3), nearly absent in the initial blend, become intense at 260 °C and then fade off at 270 °C. The Ny6 oligomers with terephthalic acid end groups (labeled **V** in Figure 4 and in Scheme 3), which are not present in the physical blend, go through a maximum at 270 °C and then disappear at 280 °C. Finally, the intensity of the copoly(esteramide) oligomers (labeled as **III** in Figure 4 and in Scheme 3) increases steadily from 260 up to 280 °C.

Therefore, the combined evidence derived from the ^{13}C NMR and MALDI analysis, nicely supports the reaction mechanism (Schemes 3 and 4) proposed for the exchange reactions in Ny6/PBT blends.

Copolymer Composition. The determination of the molar fraction of dyads (C_D) and triads (C_T), average

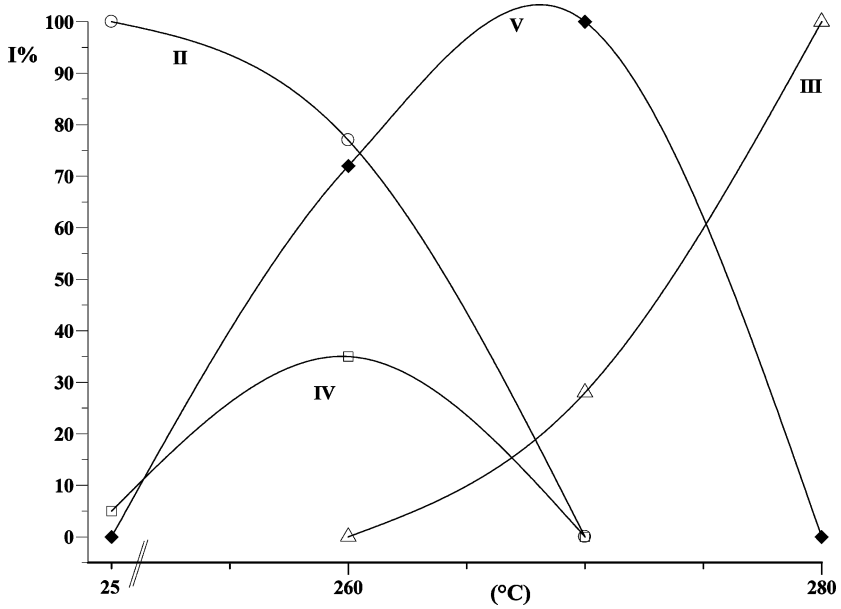


Figure 4. Normalized intensity/temperature profiles from the MALDI spectra reported in Figure 3. Species **II**, **III**, **IV**, and **V** (Scheme 3) identify in this case the peaks $A_{10,0}$, $B_{5,2}$, $C_{10,0}$, and $B_{9,0}$, respectively, in Table 3.

Table 4. Molar Fraction of Dyads, Average Sequence Lengths of B−T and CL−CL Units, and Degree of Randomness (*B*) Calculated from ^{13}C NMR Spectra of the Copolymers Formed in the Melt-Mixed Ny6/PBT−COOH Blends

temp (°C)	time (min)	molar fraction of dyads[a]				average sequence lengths[b]		
		F_{B-T}	F_{CL-B}	F_{T-Cl}	F_{Cl-CL}	B−T	CL-CL	B[c]
260	60	0.49	0.05	0.06	0.47	8.3	8.3	0.22
270	60	0.39	0.11	0.13	0.38	4.5	3.9	0.48
280	30	0.33	0.2	0.24	0.27	2.1	2.5	0.88
280	60	0.30	0.23	0.23	0.27	2.2	2.2	0.9
280	120	0.26	0.24	0.24	0.26	2.1	2.1	0.96

[a] $F_{B-T} = (A_\alpha - {}^1/_2A_{\alpha'}/A_\alpha + A_{\alpha'})C_{BT}$; $C_{CL-B} = (2A_{d'}/A_d + A_{d'} + A_{d''})C_{CL}$; $F_{T-CL} = (2A_{d''}/A_d + A_{d'} + A_{d''})C_{BT} = 2(A_{\epsilon''} + A_{\epsilon'''}/A_\epsilon + A_{\epsilon'} + A_{\epsilon''} + A_{\epsilon'''})C_{BT}$; $F_{CL-CL} = (A_d/A_d + A_{d'} + A_{d''})C_{CL}$; where A_ϵ, $A_{\epsilon'}$, $A_{\epsilon''}$, $A_{\epsilon'''}$, A_d, $A_{d'}$, $A_{d''}$, A_α, and $A_{\alpha'}$ indicate the area of the peaks ϵ, ϵ', ϵ'', ϵ''', d, d′, d″, α, and α′, respectively, in the ^{13}C NMR spectra. [b] B−T = $(1/F_{CL-B})C_{BT}$; CL-CL = $(1/F_{T-CL})C_{CL}$. [c] $B = F_{CL-B}/C_{BT} + F_{T-CL}/C_{CL}$.

sequence length (N_D, N_T) and degree of randomness (B) of the Ny6-PBT copoly(esteramide)s resulting from exchange reactions between Ny6 and PBT−COOH has been performed by ^{13}C NMR using appropriate statistical methods.[12]

Using the relative intensities of the carbon peaks d, d′, d", α, α″, ϵ, ϵ', ϵ'', and ϵ''', in Figure 2b, we have calculated (Table 4) the molar fraction of dyad sequences B−T, B−CL, CL−T, and CL-CL, the average sequence length of BT and CL units, and the degree of randomness in the copolymers obtained by heating equimolar Ny6-PBT blends. The ^{13}C NMR spectra allow also calculating (Table 2S) the same quantities from the triads centered on the terephthalic unit (B−T−B, CL−T−B, and CL−T−CL), using the intensity of peaks ϵ, ϵ', ϵ'', and ϵ''' as well as in Figure 2b.

The degrees of randomness listed in Tables 4 and 2S indicate that random copolymers were obtained only when Ny6/PBT−COOH blends were heated at 280 °C. The data may also indicate that the blends heated at 260 and 270 °C are mixtures of unreacted homopolymers and of copoly(esteramide)s (this is firmly deduced from the MALDI−MS data shown below).

However, from the analysis of the proton and carbon NMR spectra, it is impossible to estimate the relative amounts of homopolymers and copolymer in these blends. The values calculated in Tables 4 and 2S are relative to all the mixture and, since NMR is an averaging technique, is not possible to distinguish the single components and to determine accurately the quantities C_D, C_T, N_D, N_T, and B.[1−4] Better results would be obtained by performing a fractionation of the reacted blends, to separate the copoly(esteramide) from the unreacted homopolymers. However, in the present case no suitable solvent for this fractionation was found. Instead, using the MACO4 algorithm,[18−21] a detailed characterization of the copoly(esteramide)s was obtained from the analysis of the MALDI spectra in Figure 3. Chain statistics allows the characterization of any arrangement of comonomer units along the chain and gives the possibility of building theoretical mass spectra that can be compared with the experimental spectra. From the normalized intensity of peaks in Figure 3a−c, the MACO4 program calculated (Table 5) the chemical composition of the copoly(esteramide), the probability matrix (Pmatrix), the molar fraction of each oligomer sequence, the average sequence lengths of ϵ-caprolactame (CL) and butyleneterephthalate units B−T), and the degree of randomness (B). The calculation of the exchange level (copolymer yield, Table 5) was also possible from the whole MALDI spectra of the Ny6/PBT−COOH melt-mixed materials. In particular, the sum of the intensities of all the MALDI peaks in each spectrum was compared with the sum of the intensities of the MALDI peaks corresponding only to Ny6 homopolymers. From the data in Table 5, it can be seen that, at 260 °C, about half of the sample is made of copolymer. At 270 °C the copolymer yield is 80%, whereas at 280°C the homopolymers are missing.

For the determination of composition and sequence in copolymers by MS techniques, one needs only to consider the relative intensity of the co-oligomers of the same length, and the assumption that the relative peak intensities reflect the relative co-oligomers abundance has been found to be valid.[1−4,18−21] Therefore, to determine the composition and sequence of Ny6/PBT copoly-

Table 5. Yield of Copoly(esteramide), Copolymer Composition, P-Matrix Elements, Molar Fraction of Dimers, Number Average Sequence Length, and Degree of Randomness (*B*), Calculated from the MALDI Spectra of Ny6/PBT−COOH Blends

temp (°C)	time (min)	yield[a] (%)	composition C_{CL}/C_{BT}	**P**-matrix elements				molar fraction of dimers[b]				average sequence lengths		
				P_{CL-CL}	P_{CL-BT}	P_{BT-CL}	P_{BT-BT}	F_{CL-CL}	F_{CL-BT}	F_{BT-CL}	F_{BT-BT}	CL−CL	B−T	B[c]
260	60	50	0.92/0.08	0.97	0.026	0.30	0.70	0.89	0.03	0.03	0.06	38.3	3.5	0.324
270	60	80	0.86/0.14	0.84	0.16	0.99		0.72	0.14	0.14		6.2	1.0	1.16
280	60	100	0.51/0.49	0.44	0.56	0.58	0.42	0.22	0.29	0.29	0.20	1.8	1.7	1.15

[a] Yield of copolyesteramide formed in the blends after heating. [b] $F_{CL-CL} = P_{CL-CL}C_{CL}$; $F_{CL-BT} = P_{CL-BT}C_{CL}$; $F_{BT-CL} = P_{BT-CL}C_{BT}$; $F_{BT-BT} = P_{BT-BT}C_{BT}$. [c] $B = P_{BT-CL} + P_{CL-BT}$.

(esteramide)s, the calculations were performed excluding peaks $A_{n,0}$ and $B_{n,0}$ in Figure 3a−c, and using only the peaks $A_{n,m}$ and $B_{n,m}$ related to the copoly(esteramide). In fact, the presence of Ny6 or PBT oligomers due to unreacted Ny6 and PBT chains, might contribute to the intensity of $A_{n,0}$ and $B_{n,0}$ peaks. The results of the calculations obtained by the MACO4 program are collected in Table 5. It can be noted that the copoly(esteramide)s contain 92 mol % of Ny6 after 60 min of heating at 260 °C and 86 mol % of Ny6 after 60 min at 270 °C. After 60 min of heating at 280 °C, the copoly(esteramide) has a composition close to that of initial blend composition (equimolar). The degree of randomness (Table 5) increases with the processing temperature, whereas the average sequence length values indicate the formation of a block copolymer at 260 °C, the formation of a segmented copolymer at 270 °C, and finally the formation of a true random copolymer at 280 °C.

The results show that random copolymers were also obtained for blends heated at 280 °C for 30 and 120 min, in agreement with the results obtained by NMR (Tables 4 and 2S). Data in Table 5 show conclusively that in the Ny6/PBT exchange (Scheme 3), the copolymer composition is dependent on the extent of reaction, as expected in the case of a reactive blending process where initially only one of the two homopolymers has reactive chain ends.[1−4]

Conclusions

We have produced a detailed study of the chemical reactions involved in the reactive blending of Ny6 and PBT.

Summarizing the results presented here, a combined NMR and MALDI−MS analysis of the reaction products has allowed the identification of structure, composition and sequence distribution of the Ny6/PBT copoly(esteramide)s produced in the exchange.

Our results reveal the essential role of carboxyl end groups in the exchange reaction, and allow drawing a detailed mechanism for this reaction.

Furthermore, the copolymer composition was found to depend on the extent of the exchange reaction, as expected (from our kinetic model[1−4]) for the case of a reactive blending process where initially only one of the two homopolymers has reactive chain ends.

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. Many thanks are due to Mr. Roberto Rapisardi and to Mr. Gaetano Pastorelli for their continuous and skilful technical assistance.

Supporting Information Available: Table 1S, ^{1}H and ^{13}C NMR assignments of Nylon-6 (Ny6), poly 1,4-butileneterephthalate (PBT), poly(hexamethylene terephthalate) (Ny6T), *alt*-copoly(esteramide) (CL−B−CL−T) and model **A**, Table 2S, fraction of triads centered on the terephthalic units (T), average sequence lengths, and degree of randomness calculated from ^{13}C NMR spectra of Ny6/PBT−COOH blends, Figure 1S, ^{13}C NMR spectra of high molar mass Ny6/PBT blends heated for 1 h at (a) room temperature and (b) 290 °C, and Figure 2S, enlarged section of MALDI spectra of (a) Ny6 and (b) PBT−COOH samples, where peak assignments arereported in Table 3. This material is available free of charge via the Internet at http://pubs.acs.org.

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) Puglisi, C.; Samperi, F.; Di Giorgi, S.; Montando, G. *Macromolecules* **2003**, 36, 1098−1107.
(3) Montaudo, G.; Puglisi, C.; Samperi, F. *Macromolecules* **1998**, *31*, 650−661 and references therein.
(4) Montaudo, G.; Montaudo, M. S.; Scamporrino, E.; Vitalini, D. *Macromolecules* **1992**, *25*, 5099−5107.
(5) Watanabe, K.; Izuka, A.; Sumita, K.; Kita, M. *Campelloy* **1990**, 90.
(6) Fakirov, S.; Evstatiev, M.; Petrovich, S. *Macromolecules* **1993**, *26*, 5219.
(7) Evstatiev, M.; Schultz, J. M.; Petrovich, S.; Georgiev, G.; Fakirov, S.; Friedrich, K. *J. Appl. Polym. Sci.***1998**, *67*, 723.
(8) Fakirov, S.; Evstatiev, M.; Schultz, J. M. *Polymer* **1993**, *34*, 4669.
(9) Chiou, K. C.; Chang, F. C. *J. Polym. Sci., Polym. Phys. Ed.* **2000.** 38, 23.
(10) An, J.; Ge, J.; Liu, Y. *J. Appl. Polym. Sci.* **1996**, *6*, 1803.
(11) Jin, X. M.; Li, W. *J. Macromol. Sci. Rev. Macromol. Chem. Phys.* **1995**, C35, 1.
(12) Devaux, J.; Godard, P.; Mercier, J. P. *J. Polym. Sci.: Polym. Phys. Ed.* **1982**, 20, 1875. Devaux J. In *Transreactions in Condensation Polymers*; Fakirov, S., Ed.; Wiley-VCH: New York, Chapter 3, p 125, and references therein.
(13) Kricheldorf, H. R.; Leppert, E.; Schilling, G. *Makromol. Chem.* **1975**, *176*, 81.
(14) Schilling, G.; Kricheldorf, H. R. *Makromol. Chem.* **1975**, *176*, 3341.
(15) Kricheldorf, H. R.; Muehlhaupt, R. *Angew. Makromol. Chem.* **1977**, *65*, 185−192.
(16) Kricheldorf, H. R.; Hull, W. E. *J. Macromo. Sci., Chem.* **1977**, A11, 2281−2292.
(17) Kricheldorf, H. R. *Pure Appl. Chem.* **1982**, *54*, 467.
(18) Montaudo, M. S.; Montaudo, G. *Macromolecules* **1992**, *25*, 4264−4280.
(19) Montaudo, M. S.; Puglisi, C.; Samperi, F.; Montaudo, G. *Macromolecules* **1998**, *31*, 8666−8676.
(20) 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.
(21) 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.

(22) Puglisi, C.; Samperi, F.; Alicata, R.; Montando, G. *Macromolecules* **2002**, 35, 3000−3007.
(23) Alicata, R.; Montando, G.; Puglisi, C.; Samperi, F. *Rapid Commun. Mass Spectrom.* **2002**, *16*, 248−260.
(24) Paredes, N.; Casas, M. T.; Puiggali, J. *Macromolecules* **2000**, *33*, 9090.
(25) Rossbach, V.; Niessen, D.; Zahn, H. *Angew. Makromol. Chem.* **1975**, 42.
(26) Pätzold, *Angew. Chem., Int. Ed.* **1975**, *12*, 604.
(27) Jabarin, S. A.; Lofgren, E. A. *J. Appl. Polym. Sci.* **1984**, *24*, 5315−5335.
(28) Inoshita, K.; Terekawa, M.; Yasuda, T. Japan Patent 7228916, 1972.
(29) Samperi, F.; Puglisi, C.; Alicata, R.; Montando, G. *Polym. Degr. Stab.* **2003**, in press.

MA0346153