

# Mechanism of Exchange in Polyesters. Composition and Microstructure of Copolymers Formed in the Melt Mixing Process of Poly(ethylene terephthalate) and Poly(ethylene adipate)

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**ABSTRACT:** A study of the microstructure of the copolyesters formed in the exchange reactions which occur during the melt mixing of poly(ethylene adipate) (PEA) and poly(ethylene terephthalate) (PET) is reported. A PET sample stripped of the low molecular weight oligomers was melt-mixed with an equimolar amount of an PEA sample, and the exchange kinetics at 290 °C was followed by analyzing the reaction mixture by <sup>1</sup>H NMR and FAB-MS. Mass spectra of partially aminolyzed melt-mixed samples were also examined. The copolyester initially formed in the exchange reaction proved to be a block copolymer containing an excess of EA units, as expected for a reaction proceeding by the attack of PEA on the PET chains. In the later stages of the exchange reaction, the copolyester microstructure was observed to approach a Bernoullian distribution and equimolar composition. The determination of the composition and microstructure of the copolyesters formed was attempted by NMR and mass spectra of the melt-mixed samples. This proved to be a difficult task by 200-MHz <sup>1</sup>H NMR spectroscopy, since only dyads were detected here because of the large repeating units in the copolymer. Instead, the FAB mass spectra showed series of oligomers up to the octamers, and the composition and microstructure of the copolyesters was monitored by applying some methods of statistical modeling of mass spectra of copolymers.

## Introduction

In recent years considerable interest has arisen in the study of reactive blending of polyesters and in the exchange reactions which may occur during the melt mixing processes.<sup>1-8</sup>

The formation of copolyesters by this route is well-known,<sup>1-8</sup> although only recently finer mechanistic features of the exchange reactions involved have begun to be unveiled. The subject has been recently reviewed,<sup>1-3</sup> and only alcoholysis (among the three possible processes: alcoholysis, acidolysis, ester-ester exchange) is believed to occur. The kinetics of exchange reactions in polyesters has been followed by NMR<sup>4</sup> and MS techniques,<sup>5,7</sup> and the presence of mixed oligoesters among the reaction products of mixtures of homopolyesters has been demonstrated.<sup>5</sup> The temperatures necessary to activate the exchange process in polyesters (about 250–300 °C) are also sufficient to activate ring-chain equilibration reactions (the equilibrium being shifted in favor of the rings at these temperatures).<sup>9,10</sup> The formation of cyclic compounds is therefore what one should expect if a thermal reaction proceeds through macrocyclization processes involving ester-exchange reactions. In fact,<sup>9,10</sup> ester-exchange reactions in polyesters lead in most cases to the formation of cyclic esters, which have been ascertained to be the primary reaction products also for PEA<sup>11</sup> and PET.<sup>12,13</sup>

Recently,<sup>6</sup> neutron-scattering studies have ascertained that the rate of exchange in PET is molecular weight dependent, thus hinting that the exchange proceeds through a mechanism involving active chain ends.

We have now succeeded in performing an experiment where a PET sample, completely freed from all the low molecular weight oligomers up to a mass of about 2000 Da (as monitored by FAB mass spectrometry<sup>14-17</sup>), was melt-mixed with an equimolar amount of an unfractionated PEA sample, and the exchange kinetics at 290 °C was

followed by analyzing the melt mixture, at different reaction times, by <sup>1</sup>H NMR spectroscopy and by FAB-MS.

We observed that the copolyester initially formed in the exchange reaction is a block copolymer containing an excess of adipic (EA) units, as it should be expected if the reaction would proceed through the attack of PEA oligomers on the macromolecular PET chains. The results obtained from the mass spectra of the partially aminolyzed melt-mixed samples confirm this conclusion. In the later stages of the exchange reaction, the copolyester microstructure was observed to approach a random distribution and equimolar composition.

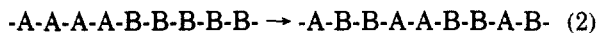
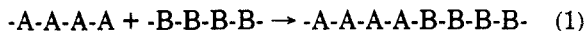
Following these changes proved to be a difficult task by 200-MHz <sup>1</sup>H NMR spectroscopy, since only dyads were detected here because of the large repeating units present in the copolymer (see below).

On the contrary, FAB-MS was successfully used to identify the low molecular weight oligomers present in the polymeric material.<sup>16,17</sup> When the material possesses too high dimensions to be detected by mass spectrometers (having usually cut-off below 10 000), the MS analysis may be performed on the partial degradation products of the macromolecules. In our case, the mass spectra of the melt-mixed samples and of their aminolyzed derivatives showed series of low molecular weight oligomers up to octamers.

Monitoring the composition and microstructure of the copolyester formed was possible by the application of some methods of statistical modeling of mass spectra of copolymers recently introduced.<sup>18-21</sup>

## Theory

It is convenient to describe the ester-exchange reactions, which lead to the formation of copolymer molecules, as the result of two concurring processes: the formation of the copolymer from homopolymers (eq 1) and the process



in which the copolymer rearranges itself in another copolymer (eq 2), with a different sequence of A and B units along the copolymer chain.

NMR and mass spectrometry are useful analytical tools for the investigation of exchange reactions, due to their ability to estimate separately the abundance of the left-side species and that of the right-side species in eqs 1 and 2. Thus, if one records the spectra of the PEA-PET mixtures as the exchange reaction proceeds, two separate effects are seen: the process in eq 1 causes the intensity of signals associated with homopolymer segments to decrease with respect to the sum of the intensities of copolymer segments; the process in eq 2 causes the pattern described by the peaks associated with copolymer segments to change its shape (see below). Thus, the inspection of the NMR or mass spectra of a melt-mixed sample (made of three components: two homopolymers and the formed copolymer) should allow one to draw conclusions about the occurrence of the exchange reaction. Another interesting feature of the reaction in eqs 1 and 2 is that, even if they occur in a closed system (where the sample composition is constant), the composition of the resulting copolymer may deviate from the value given by the molar ratio of the two homopolymers present. In order to put into evidence the difference, it is necessary to measure both the sample composition and the composition of the copolymer.

Two different methodologies<sup>19</sup> can be used in the analysis of NMR or mass spectra of a mixture of two polymers undergoing exchange processes: the first approach (data partitioning) considers the exchange reaction as a whole (eqs 1 and 2), the second (data best-fitting) focuses exclusively on the modifications of the reaction products depicted in eq 2. In the data-partitioning approach the experimental peak intensities are partitioned in various groups, each group having a different number of units in the sequence (dyads, triads, etc., in NMR spectroscopy) or different size (dimers, trimers, tetramers, pentamers, etc., in MS). Taking a linear combination of the experimental intensities belonging to each of these groups, it is possible to obtain a first characterization of the sample. Each group of peaks yields an independent estimate of the molar fraction of comonomer A in the sample ( $s_A$ ) and in the copolymer ( $c_A$ ).<sup>19</sup> These values can be mediated in order to obtain an average estimate. In the case of MS, we have

$$s_A = \sum_y 1/\alpha_y [\sum_m \sum_n n \delta_{m+n,y} I_{A_m B_n}] \quad (3)$$

$$c_A = \sum_y 1/\beta_y [\sum_m \sum_n n \delta_{m+n,y} (1 - \delta_{n,y}) (1 - \delta_{m,y}) I_{A_m B_n}] \quad (4)$$

where  $I_{A_m B_n}$  is the mass spectral intensity associated with the oligomer  $A_m B_n$  and  $\delta$  is the Kronecker symbol ( $\delta_{i,j} = 1$  if  $i = j$ ,  $\delta_{i,j} = 0$  otherwise). The quantities  $\alpha_y$  and  $\beta_y$  are the sum of the intensities of peaks having degree of polymerization  $y$ .  $\alpha_y$  is computed by taking into account homooligomer peaks, whereas  $\beta_y$  is computed without those peaks. The corresponding equations for NMR are obtained from eqs 3 and 4 with slight modifications.

In the absence of information on higher sequences, peak intensities corresponding to dimers (MS) or dyads (NMR) can be also used to evaluate the sample number average length of like monomers,  $\langle d_A \rangle$  and  $\langle d_B \rangle$ , which represent a measure of the degree of "blockiness" in the sample:

$$\langle d_A \rangle = (I_{A_2} + 1/2 I_{AB}) / (1/2 I_{AB}) \quad (5)$$

$$\langle d_B \rangle = (I_{B_2} + 1/2 I_{AB}) / (1/2 I_{AB}) \quad (6)$$

The latter may yield an estimate of the number average length of like monomers,<sup>22</sup>  $\langle n_A \rangle$  and  $\langle n_B \rangle$ , in the copolymer, provided that the data in eqs 7 and 8 are available, where

$$\langle n_A \rangle = (\langle d_A \rangle - f_1 M_n^A) / f_3 \quad (7)$$

$$\langle n_B \rangle = (\langle d_B \rangle - f_2 M_n^B) / f_3 \quad (8)$$

$M_n^A$  and  $M_n^B$  are the number average degree of polymerization of homopolymers A and B and where  $f_1$ ,  $f_2$ , and  $f_3$  are, respectively, the molar fractions of homopolymer A, homopolymer B, and of the copolymer in the mixture.

In the case of pure copolymers,  $\langle n_A \rangle$  and  $\langle d_A \rangle$  coincide, but they differ in the case of mixtures generated in ester-exchange processes. The number average lengths of like monomers in the sample,  $\langle d_A \rangle$  and  $\langle d_B \rangle$ , do not follow a simple pattern as the exchange reaction proceeds and, for this reason,  $\langle d_A \rangle$  and  $\langle d_B \rangle$  provide little information.

On the other hand, thermodynamics requires that  $\langle n_A \rangle$  and  $\langle n_B \rangle$  decrease steadily as the exchange reaction proceeds. In fact, copolymer chain configurations exhibiting a large number of consecutive A or B units (and therefore representing highly ordered configurations), have a lower entropy with respect to chain configurations in which A and B units are found randomly along the chain.

Finally, in the data-partitioning approach each group of peaks in the spectrum yields an independent estimate of the extent of exchange ( $EE_y$ ), which measures the amount of copolymer formed in the reaction (eq 1) between the two homopolymers:

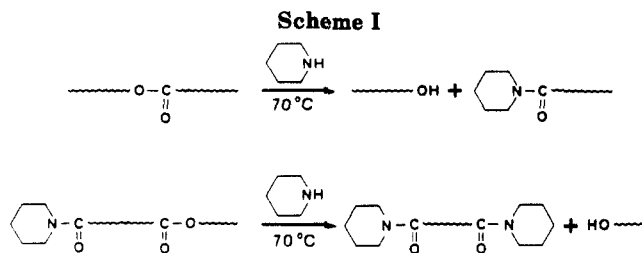
$$EE_y = \beta_y / [\alpha_y (1 - I_y^{\text{LIMIT}})] \quad (9)$$

The quantities  $EE_y$  in eq 9 vary within 0 and 1. In cases where  $EE_y = 1$ , the abundance of homooligomers,  $I_y^{\text{HOMO}}$ ,  $= \alpha_y - \beta_y$  never drops to zero, but remains always above a limiting value,  $I_y^{\text{LIMIT}}$ , which represents the sum of the homooligomer intensities for a rigorously random copolymer. Thus<sup>22</sup> we have

$$I_y^{\text{LIMIT}} = [c_A]^y + [c_B]^y \quad (10)$$

As stated above, in order to monitor the rearrangements occurring in the structure of the reaction products (eq 2), the best-fitting method can be used. In this approach, the peak intensities corresponding to homopolymers are completely neglected, since the only peaks directly related to the microstructure of the copolymer<sup>18,19</sup> are the copolymer peaks.

The statistical analysis of copolymers makes use of the Markoffian model in order to characterize the microstructure of copolymer samples, and when a theoretical distribution is assumed and the calculated abundances are fit with the experimental peak intensities, the copolymer composition can be determined.<sup>18,19,22</sup> According to



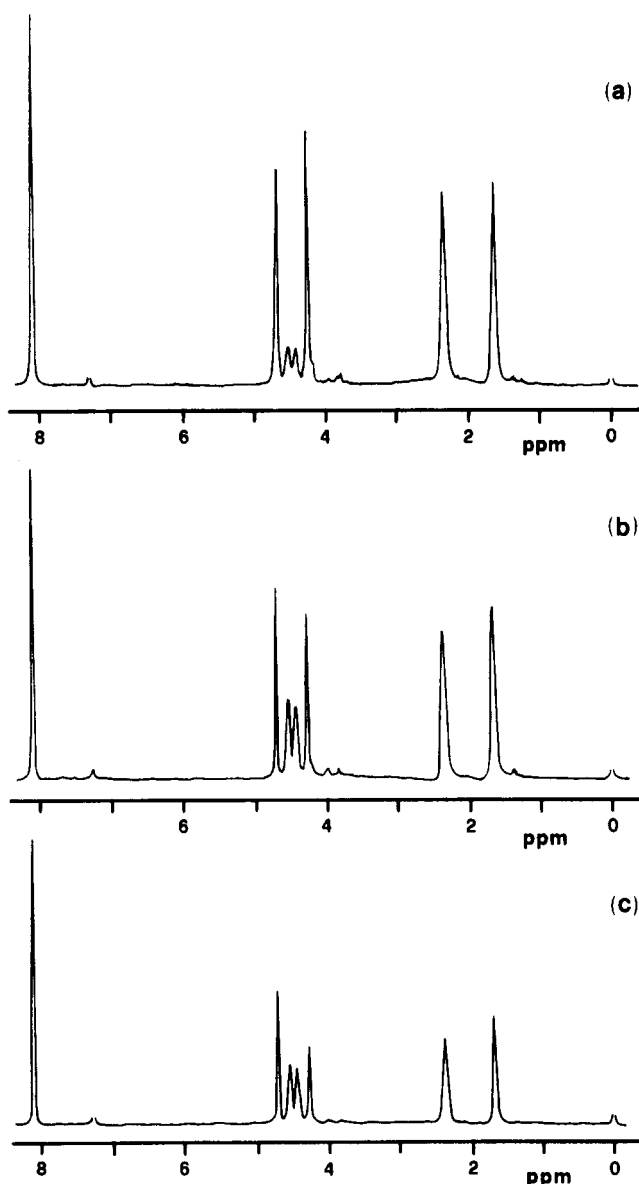


Figure 1. 200-MHz  $^1\text{H}$  NMR spectra, recorded in  $\text{CDCl}_3$ , of PEA-PET samples melt-mixed at  $290^\circ\text{C}$  for (a) 20 min, (b) 60 min, and (c) 270 min. The truncated peaks are due to TMS and  $\text{CHCl}_3$ .

Table I  
Results of the Analysis on  $^1\text{H}$  NMR Spectra of the PEA-PET Melt-Mixed Samples

sample	rel intens <sup>a</sup>			$s_{\text{EA}}^b$	$\langle d_{\text{EA}} \rangle^c$	$\langle d_{\text{ET}} \rangle^c$
	EA-EA	EA-ET	ET-ET			
M20	43.8	17.2	39.0	52	8.3	10.0
M60	26.8	47.5	25.7	51	2.0	2.2
M270	22.0	50.5	27.5	46	2.2	1.7

<sup>a</sup> Relative intensities of EA-EA, EA-ET, and ET-ET dyads in the  $^1\text{H}$  NMR spectra of the melt-mixed samples. <sup>b</sup> Calculated<sup>8</sup> molar fractions of EA in the melt-mixed samples. <sup>c</sup> Calculated sample number average lengths (eqs 5 and 6).

chain statistics, the sequence distribution of a two-component copolymer is completely defined when the four elements ( $P_{xy}$ ) of the probability matrix are determined. The latter are linked by the following normalization conditions:

$$P_{\text{AA}} + P_{\text{AB}} = 1 \quad P_{\text{BB}} + P_{\text{BA}} = 1 \quad (11)$$

Each Markoffian theoretical distribution has an associated composition and an associated number average length of like monomers<sup>23</sup> which are given by

$$c_{\text{A}} = P_{\text{BA}} / (P_{\text{AB}} + P_{\text{BA}}) \quad (12)$$

$$\langle n_{\text{A}} \rangle = 1/P_{\text{AB}} \quad \langle n_{\text{B}} \rangle = 1/P_{\text{BA}} \quad (13)$$

As a consequence of neglecting the peak intensities corresponding to homopolymers, in this approach it is not possible to obtain the sample compositions  $s_{\text{A}}$  and  $s_{\text{B}}$ , neither the sample number average lengths of like monomers  $\langle d_{\text{A}} \rangle$  and  $\langle d_{\text{B}} \rangle$ .

The statistical approach allows the introduction of a definition of the extent of exchange alternative to eqs 9 and 10, which is directly related to the copolymer P-matrix elements:

$$\text{EE} = P_{\text{AB}} + P_{\text{BA}} \quad \text{if} \quad P_{\text{AB}} + P_{\text{BA}} < 1$$

$$\text{EE} = 2 - P_{\text{AB}} + P_{\text{BA}} \quad \text{if} \quad P_{\text{AB}} + P_{\text{BA}} > 1 \quad (14)$$

The quantity  $P_{\text{AB}} + P_{\text{BA}}$  is the degree of randomness<sup>8,23</sup> ( $R$ ) of the copolymer. When  $R$  is close to 0, the copolymer has long blocks of A and B units, whereas when  $R = 1$ , A and B units are found randomly along the chain and when  $R = 2$ , the copolymer is exactly alternating.

## Experimental Section

**Materials.** Basic materials were commercial products appropriately purified before use.

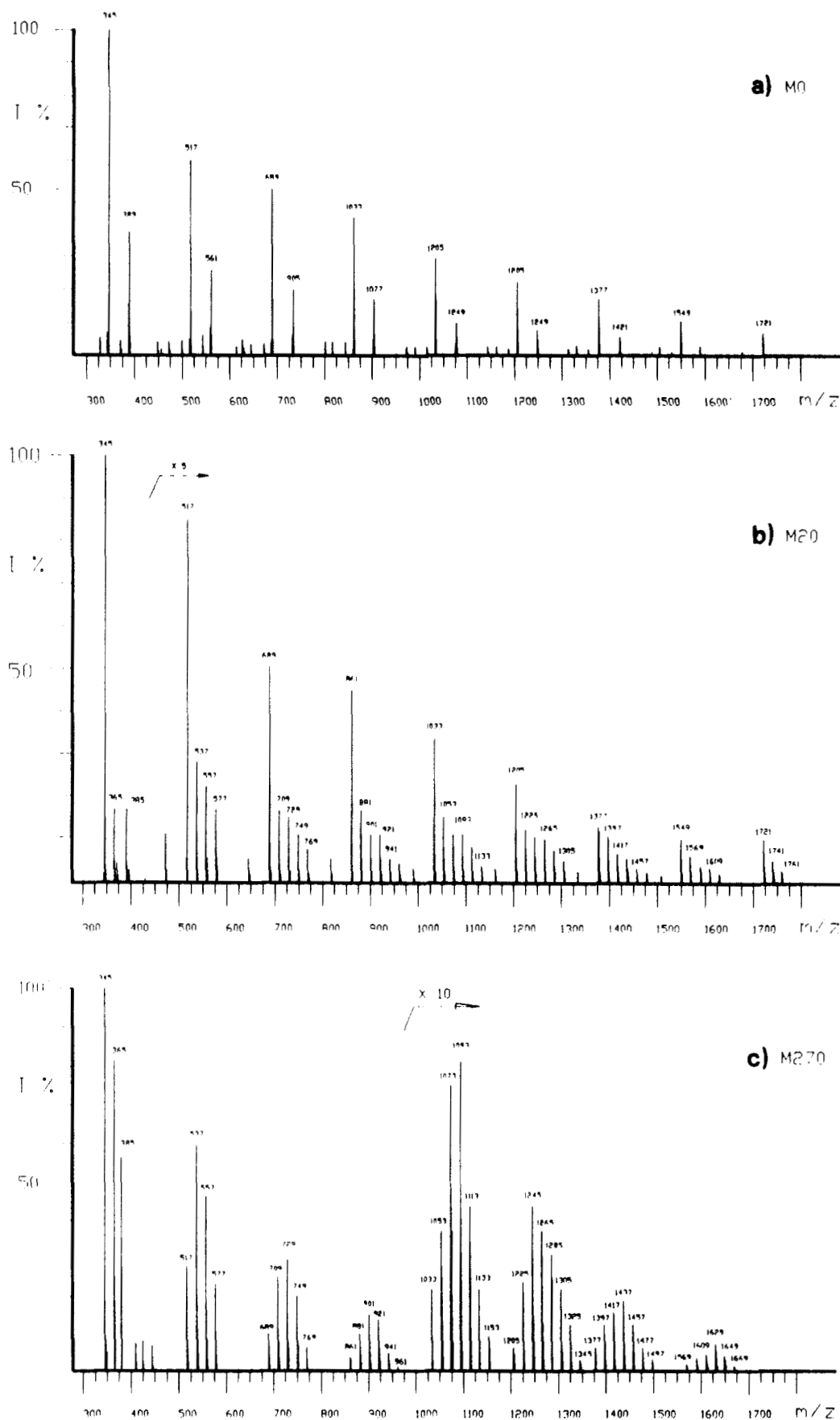
**Polymer Synthesis.** Poly(ethylene terephthalate) (PET) and poly(ethylene adipate) (PEA) were synthesized by dispersion polycondensation starting from ethylene glycol and terephthaloyl or adipoyl chloride. The procedure adopted for PET is here reported. A 2.2-g (0.032-mol) amount of ethylene glycol and 6.8 g (0.064 mol) of  $\text{Na}_2\text{CO}_3$  in 25 mL of  $\text{H}_2\text{O}$  were placed in a pre-cooled Waring blender. To the rapidly stirred solution was added 6.5 g (0.032 mol) of terephthaloyl chloride in 25 mL of THF in one application. The mixture was stirred for 5 min and poured into about 400 mL of cold water. After some hours, the residue was filtered and washed with water. The polymeric material was completely stripped of the low molecular weight oligomers (as evidenced by its GPC trace and FAB mass spectrum) by repeated treatments with boiling THF and dried under vacuo at  $70^\circ\text{C}$ . The yield was about 55%. In the PEA case, the polyester still contained moderate amounts of oligomers (GPC trace); the yield was about 65%.

**Copolyester Formation.** The copolyesters containing both terephthalic and adipic units were obtained by heating a powdered equimolar mixture of the two homopolyesters in separate sealed (under vacuum) glass tubes at  $290^\circ\text{C}$  for different times: 10, 20, 30, 45, 60, 90, 120, and 270 min. The resulting products will be indicated as M10, M20, M30, M45, M60, M90, M120, and M270 (as M0 will indicate the original PEA/PET mixture).

**Partial Aminolysis.** Aminolysis was performed on 20 mg of each melt-mixed sample dissolved in 2 mL of nitrobenzene, by adding 0.5 mL of piperidine to each solution stirred under nitrogen atmosphere at  $70^\circ\text{C}$ . After 6 h, the solvent and the unreacted piperidine were removed under  $\text{N}_2$  flow and the resulting aminolysis<sup>24</sup> products (Scheme 1), labeled as P10, P30, P60, P120, and P270, were dried under vacuo at  $70^\circ\text{C}$ .

**GPC Analysis.** A Waters 6000A apparatus, equipped with four  $\mu$ -Styragel columns (in the order 1000-, 500-, 10000-, and 100-Å pore size), attached in series, was used. The analyses were performed at  $25^\circ\text{C}$  using  $\text{CHCl}_3$  as eluant at a flow rate of 1 mL/min.

**FAB-MS Analysis.** FAB analyses were performed on a double-focusing Katos MS50S mass spectrometer equipped with the standard FAB source. The FAB gun was operated with a 7-8-keV xenon beam. The instrument was scanned from  $m/z$  3000 to 30, with a scan rate of 30 s/decade. The accelerating voltage was 8 kV. The mass resolution was approximately 3000. Mass spectra were recorded using an UV recorder. Spectra were obtained using 3-nitrobenzyl alcohol (TNB) as a matrix. Peak intensity values shown in the mass spectra represent the average



**Figure 2.** Positive FAB mass spectra of (a) original PEA-PET mixture (M0), (b) sample melt-mixed for 20 min (M20), and (c) sample melt-mixed for 270 min (M270).

of at least three different runs.

**$^1\text{H}$  NMR Analysis.**  $^1\text{H}$  NMR spectra were obtained on a Bruker 200 A-CF spectrometer using  $\text{CDCl}_3$  as solvent and TMS as an internal reference.

**MACO 4 Calculations.** FAB-MS data were analyzed by using the MACO 4 program previously described.<sup>19</sup> MACO 4 accepts

as input (a) the experimental mass spectrum, (b) the mathematical model that defines the distribution of comonomers along the chain, (c) 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 nonselective or selective cleavage process. The program generates the theoretical mass spectrum

**Table II**  
**Experimental Mass Spectral Intensities for the PEA-PET Melt-Mixed Samples**

oligomer <sup>a</sup>	<i>m/z</i> <sup>b</sup>	M10	M20	M30	M45	M90	M120	M270
A <sub>2</sub> E <sub>2</sub>	345	130	350	720	9600	4550	14000	1700
AE <sub>2</sub> T	365	17	70	240	5800	2800	13000	1350
E <sub>2</sub> T <sub>2</sub>	385	15	65	220	4400	2200	8500	1000
A <sub>3</sub> E <sub>3</sub>	517	85	155	290	2700	1300	3300	450
A <sub>2</sub> E <sub>3</sub> T	537	11	50	180	3600	2100	6900	950
AE <sub>3</sub> T <sub>2</sub>	557	11	35	150	2700	1600	5000	750
E <sub>3</sub> T <sub>3</sub>	577	14	25	110	1450	800	1900	370
A <sub>4</sub> E <sub>4</sub>	689	115	95	160	170	210	160	34
A <sub>3</sub> E <sub>4</sub> T	709	15	30	110	270	162	380	40
A <sub>2</sub> E <sub>4</sub> T <sub>2</sub>	729	16	27	100	260	160	420	96
AE <sub>4</sub> T <sub>3</sub>	749	11	18	65	160	86	210	64
E <sub>4</sub> T <sub>4</sub>	769	2	14	25	50	26	60	18
A <sub>5</sub> E <sub>5</sub>	861	35	80	90	25	17	21	6
A <sub>4</sub> E <sub>5</sub> T	881	6	27	75	50	35	58	16
A <sub>3</sub> E <sub>5</sub> T <sub>2</sub>	901	6	22	65	57	38	78	24
A <sub>2</sub> E <sub>5</sub> T <sub>3</sub>	921	5	20	50	42	28	58	21
AE <sub>5</sub> T <sub>4</sub>	941	3	10	25	20	13	22	7
E <sub>5</sub> T <sub>5</sub>	961	1	9	15	6	4	4	1.5
A <sub>6</sub> E <sub>6</sub>	1033	22	65	55	7.5	6	5	2.5
A <sub>5</sub> E <sub>6</sub> T	1053	5	27	55	18.0	12.5	19	6.0
A <sub>4</sub> E <sub>6</sub> T <sub>2</sub>	1073	5	19	45	25.0	20.0	31	11.0
A <sub>3</sub> E <sub>6</sub> T <sub>3</sub>	1093	1	20	40	23.5	17.0	29	13.0
A <sub>2</sub> E <sub>6</sub> T <sub>4</sub>	1113		16	25	14.0	9.5	17	6.0
AE <sub>6</sub> T <sub>5</sub>	1133		8	15	6.0	4.5	4	2.5
E <sub>6</sub> T <sub>6</sub>	1153		6	10	1.5	1.0	1.5	
A <sub>7</sub> E <sub>7</sub>	1205	3.2	8.2	6.8	2.5	3.0	1.5	
A <sub>6</sub> E <sub>7</sub> T	1225	0.8	4.2	6.4	8.0	5.0	5.5	2.0
A <sub>5</sub> E <sub>7</sub> T <sub>2</sub>	1245	0.6	3.8	6.0	11.0	9.0	13.0	5.5
A <sub>4</sub> E <sub>7</sub> T <sub>3</sub>	1265	0.4	3.4	5.8	12.5	9.0	15.5	5.0
A <sub>3</sub> E <sub>7</sub> T <sub>4</sub>	1285		2.4	2.8	9.0	6.5	8.5	5.0
A <sub>2</sub> E <sub>7</sub> T <sub>5</sub>	1305		1.8	2.0	4.0	3.5	3.5	2.0
AE <sub>7</sub> T <sub>6</sub>	1325			1.6	2.5	1.0	1.0	
A <sub>8</sub> E <sub>8</sub>	1377	1.8	4.6	3.4		1.0		1.2
A <sub>7</sub> E <sub>8</sub> T	1397		3.6	4.0	3.0	3.5	2.0	2.0
A <sub>6</sub> E <sub>8</sub> T <sub>2</sub>	1417		2.6	4.6	4.5	4.5	4.5	2.5
A <sub>5</sub> E <sub>8</sub> T <sub>3</sub>	1437		2.2	5.4	5.5	4.5	6.0	3.7
A <sub>4</sub> E <sub>8</sub> T <sub>4</sub>	1457		1.6	4.8	4.5	4.5	6.0	3.1
A <sub>3</sub> E <sub>8</sub> T <sub>5</sub>	1477		1.4	2.0	3.0	3.0	3.0	2.5
A <sub>2</sub> E <sub>8</sub> T <sub>6</sub>	1497			1.2		1.5	1.5	0.9
AE <sub>8</sub> T <sub>7</sub>	1517					1.0		

<sup>a</sup> Composition of the cyclic oligomers in which A = -CO-(CH<sub>2</sub>)<sub>4</sub>-CO-, E = -O-(CH<sub>2</sub>)<sub>2</sub>-O-, and T = -CO-Ph-CO-. <sup>b</sup> The molecular ions of these compounds appear in the positive FAB mass spectra as (M + 1)<sup>+</sup>.

using<sup>19</sup> equation

$$I_{A_nB_n} = w(P_{AA}, P_{AB}, P_{BA}, P_{BB}) \quad (15)$$

and, 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. MACO 4 yields as output the parameters that give the best agreement and a listing of the corresponding theoretical spectrum. The difference between observed and calculated values is expressed<sup>19</sup> in terms of error by means of the Hamilton agreement factor (AF):

$$AF = q \sum_i (I_i^{\text{exp}} - I_i^{\text{calc}})^2 \quad (16)$$

where  $I_i^{\text{exp}}$  and  $I_i^{\text{calc}}$  are the normalized experimental and calculated abundances of the oligomers and where the normalization factor  $q$  is given by  $q = 1/(\sum_i (I_i^{\text{exp}})^2)^{0.5}$ . An average AF value is usually given by MACO 4 as a result of a calculation on a copolymer sample (see tables below). However, the program calculates also separate AF values for each group of oligomers that can be used to check the accuracy of the experimental data and the self-consistency of the calculations.<sup>19</sup>

## Results and Discussion

NMR data on addition copolymers usually contain information on higher sequences (sometimes up to the heptads or even higher), and therefore are the standard source to obtain the sequence distribution by statistical analysis.<sup>22,25</sup> In condensation polymers, however, the large repeating units limit the NMR resolving power, so that only lower sequences are actually observed.

**Table III**  
**Results of the Analysis on FAB-MS Spectra of the PEA-PET Melt-Mixed Samples M0-M270 According to the Data-Partitioning Approach**

sample	<i>c</i> <sub>EA</sub> <sup>a</sup>	<i>EE</i> <sup>b</sup>	<i>&lt;d</i> <sub>EA</sub> <sup>c</sup>	<i>&lt;d</i> <sub>ET</sub> <sup>c</sup>
M0	100	0		
M10	75	55	16.3	2.7
M20	57	61	11.0	3.9
M30	56	60	7.0	2.8
M45	53	77	4.3	3.5
M60	53	82	3.3	2.5
M90	53	85	2.5	2.2
M120	53	97	2.4	1.8
M270	52	95	2.2	1.8

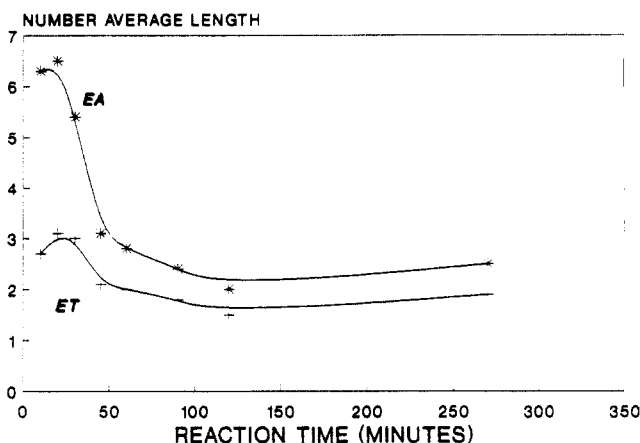
<sup>a</sup> Calculated molar fraction of EA in the copolymer by eq 4. <sup>b</sup> Calculated extent of exchange by eqs 9 and 10. <sup>c</sup> Calculated sample number average lengths by eqs 5 and 6.

In Figure 1, the <sup>1</sup>H NMR spectra of three samples obtained from the PEA-PET mixture melt-mixed at 290 °C for (a) 20 min, (b) 60 min, and (c) 270 min are reported.<sup>26</sup> In these spectra, the signal at 8.103 ppm is due to the CH aromatic hydrogen atoms of terephthalic units while the two signals at 2.353 and 1.661 ppm correspond to proton resonances of the CH<sub>2</sub> aliphatic hydrogen atoms of adipic units. The four signals observed in the region between 4 and 5 ppm are due to -O-CH<sub>2</sub>-CH<sub>2</sub>-O- units corresponding to the three possible dyads along the polymer chains. In particular, the signal at 4.258 ppm has been assigned to the proton resonance of -O-CH<sub>2</sub>-CH<sub>2</sub>-O- group between two adipic units (-EA-EA- dyads), while that at

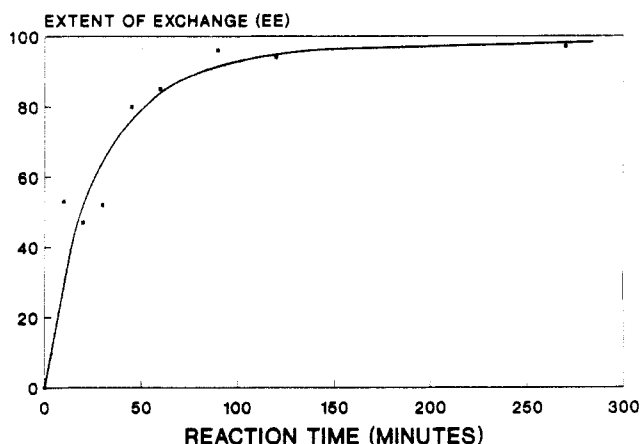
**Table IV**  
**Results of the Analysis on FAB-MS Spectra of the PEA-PET Melt-Mixed Samples Using the Best-Fitting Approach**

sample	P-matrix <sup>a</sup>	$c_{EA}/c_{ET}$ <sup>b</sup>	EE <sup>c</sup>	$\langle n_{EA} \rangle$ <sup>d</sup>	$\langle n_{ET} \rangle$ <sup>d</sup>	AF <sup>e</sup>
M0	1.00/0.00/0.00/1.00	100/0				
M10	0.84/0.16/0.37/0.63	70/30	53	6.3	2.7	20.0
M20	0.85/0.15/0.32/0.68	68/32	47	6.5	3.1	7.4
M30	0.82/0.18/0.34/0.66	65/35	52	5.4	3.0	5.4
M45	0.68/0.32/0.48/0.52	60/40	80	3.1	2.1	0.4
M60	0.65/0.35/0.50/0.50	58/42	85	2.8	2.0	0.1
M90	0.59/0.41/0.55/0.45	57/43	96	2.4	1.8	0.2
M120	0.50/0.50/0.66/0.34	56/44	94	2.0	1.5	0.8
M270	0.50/0.50/0.53/0.47	56/44	97	2.5	1.9	1.0

<sup>a</sup> First-order Markoffian P-matrix elements resulting from best-fit ( $P_{EA/EA}/P_{EA/ET}/P_{ET/EA}/P_{ET/ET}$ ). <sup>b</sup> Calculated copolymer composition (EA/ET molar ratio) using eq 12. <sup>c</sup> Calculated extent of exchange using eq 14. <sup>d</sup> Calculated number average lengths of EA and ET units in the copolymer by eq 13. <sup>e</sup> Agreement factor computed using eq 16.



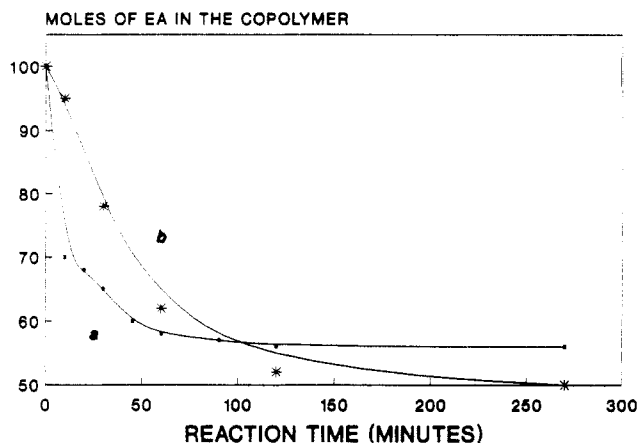
**Figure 3.** Copolymer number average lengths ( $\langle n_{EA} \rangle$  and  $\langle n_{ET} \rangle$ ), versus the reaction time.



**Figure 4.** Calculated extent of exchange versus the reaction time.

4.699 ppm has been assigned to the ethylene glycol between two terephthalic units (–ET–ET– dyads). The two central signals at 4.527 and 4.333 ppm correspond to the proton resonances of the ethylene glycol between an adipic and a terephthalic unit (–EA–ET– dyads).

The attempt to analyze these spectral data by the best-fitting approach fails because of the small number of peaks. In fact, dyad data allow the determination of the relative intensity of three sequences [(–EA–EA–), (–EA–ET–), and (–ET–ET–)], but only the signals due to EA–ET dyads correspond certainly to a copolymer structure. To calculate the composition ( $c_{EA}$ ) of the copolymer formed, these signals should be normalized against the intensity of the signals corresponding to the two homopolymers, but this is not legitimate, since the latter originate either from the EA–EA and ET–ET dyads present in the unconverted homopolymers or from the EA–EA and ET–ET dyads present in the copolymer formed. If one eliminates from



**Figure 5.** Calculated copolymer composition as a function of reaction time: (a) melt-mixed samples, (b) aminolyzed samples.

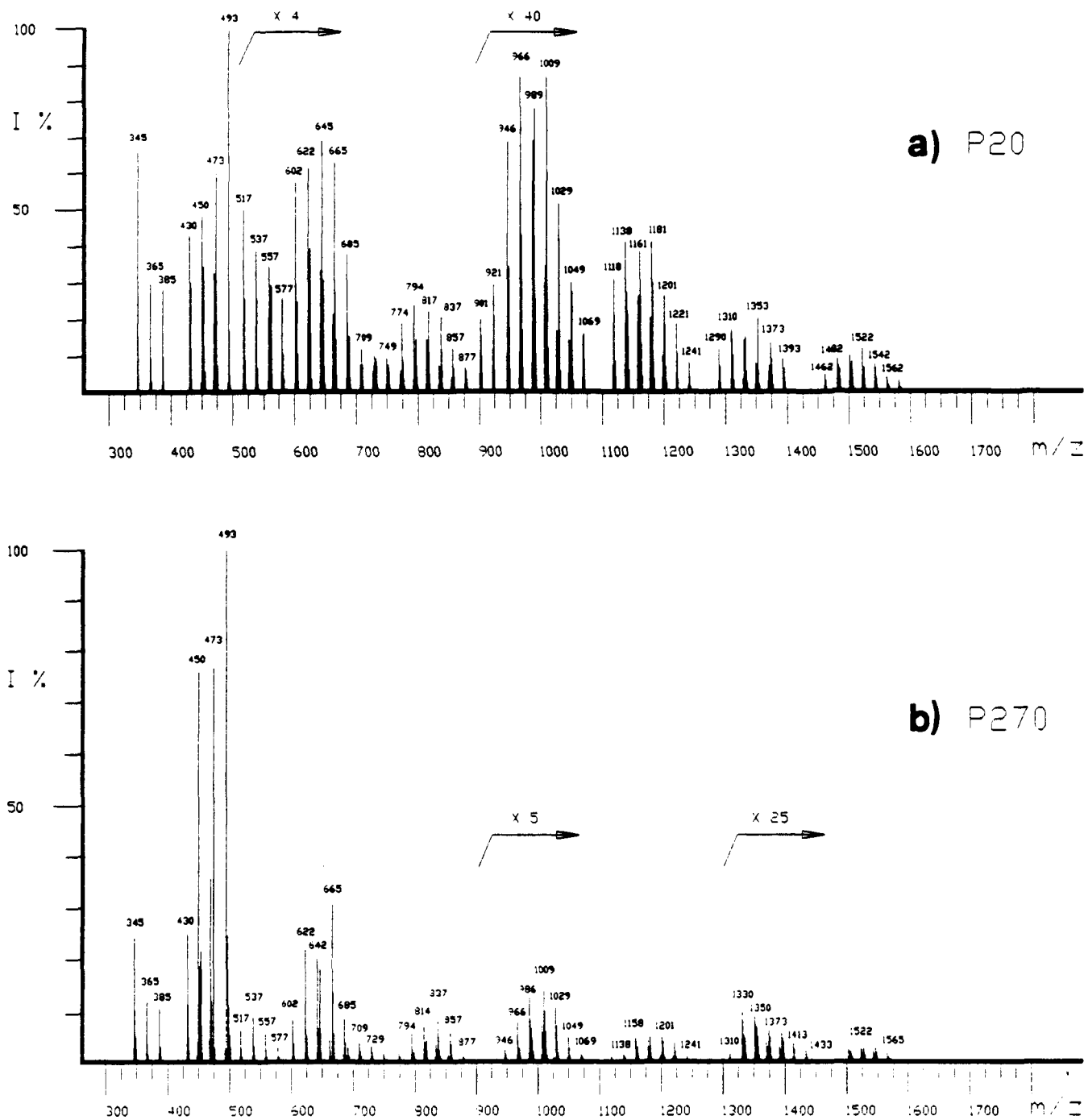
the set of data the two signals EA–EA and ET–ET, only the EA–ET signal remains and the copolymer P-matrix cannot be extracted.

As matter of fact, determinations of the degree of randomness ( $R$ ) for melt-mixed polyester samples have appeared<sup>8</sup> in the literature, using NMR dyad data. However, this procedure is not legitimate, since the peculiar properties of  $R$  refer to a pure copolymer and not to a mixture of unconverted homopolymers and copolymer.

In the present case, the determination of the copolymer composition is impossible also if the data-partitioning approach is used. In fact, this approach yields a set of average values which describe the overall properties of the system (made of the two homopolymers plus the copolyester which is gradually formed). If the intensities of the three signals EA–EA, EA–ET, and ET–ET are combined together, only an estimate of the sample composition ( $s_{EA}$ ,  $s_{ET}$ ) and of the sample number average block lengths ( $\langle d_{EA} \rangle$ ,  $\langle d_{ET} \rangle$ ) can be obtained, but not the copolymer composition ( $c_{EA}$ ,  $c_{ET}$ ) and the number average length of like monomers ( $\langle n_{EA} \rangle$ ,  $\langle n_{ET} \rangle$ ) in the copolymer. The computed values of  $s_{EA}$  and  $s_{ET}$  (Table I) remain practically constant at the value  $s_{EA}/s_{ET} = 1$  (closed system). Also the values of  $\langle d_{EA} \rangle$  and  $\langle d_{ET} \rangle$  (Table I) are almost coincident, since they refer to the sample, not to the pure copolymer.

From this analysis it follows that NMR data in Figure 1 and Table I are not useful to determine the composition and microstructure of the copolyester formed in the initial stages of the melt-mixing process, because they yield average values which include the unconverted homopolymers.

However, in later stages of the reaction, the molar fraction of homopolymers in the sample becomes negligible. Under these conditions, the values of  $s_A$ ,  $s_B$  and  $\langle d_{EA} \rangle$ ,  $\langle d_{ET} \rangle$  constitute a good approximation for the



**Figure 6.** Positive FAB mass spectra of partially aminolyzed (a) sample melt-mixed for 20 min (P20) and (b) sample melt-mixed for 270 min (P270).

copolymer compositions,  $c_{EA}$  and  $c_{ET}$ , and for the copolymer number average lengths,  $\langle n_{EA} \rangle$  and  $\langle n_{ET} \rangle$ , respectively. It was actually found that the NMR data for 270 min (Table I) are in agreement with the MS data (see below).

In Figure 2a, the positive FAB mass spectrum of the original PEA-PET mixture (sample M0) is reported. The spectrum shows the complete absence of peaks corresponding to species containing ET units (thus being very similar to that of pure PEA), since the PET in the mixture was completely freed from all the low molecular weight oligomers.

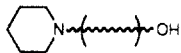
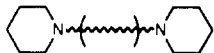
The positive FAB mass spectra shown in Figure 2b,c were obtained from M20 and M270 samples (the spectra of the other melt-mixed samples, corresponding to intermediate reaction times, have been omitted for brevity). In Table II the structural assignments for the identified peaks are reported.

The mass spectra are constituted essentially by a series of peaks (corresponding to both homo- and cooligomers) due to the protonated molecular ions of the cyclic esters. Peaks due to open-chain oligomers, not observed in the positive FAB mass spectra, were detected in the negative FAB mode (data omitted for brevity).

The MS peak intensities of each of the eight spectra were grouped according to the data-partitioning approach and these intensities were inserted in pertinent equations to obtain an estimate of the copolymer composition ( $c_{EA}$ ), of the extent of exchange (EE), and of the sample number average block lengths,  $\langle d_{EA} \rangle$  and  $\langle d_{ET} \rangle$  (Table III). The composition of the formed copolymer (Table III) shows an excess of EA units in the early stages of the reaction and then levels off nearly at equal amounts of EA and ET in the later stages.

The extent of exchange (Table III) increases with reaction time. In the last two samples (M120, M270), EE

**Table V**  
**Experimental Mass Spectral Intensities for the Aminolyzed PEA-PET Melt-Mixed Samples**

													
oligomer <sup>a</sup>	<i>m/z</i> <sup>b</sup>	P10	P30	P60	P120	P270	oligomer <sup>a</sup>	<i>m/z</i> <sup>b</sup>	P10	P30	P60	P120	P270
A <sub>2</sub> E <sub>2</sub>	430	2000	2000	1350	1700	1100	A <sub>2</sub> E <sub>1</sub>	453	1550	1550	950	1250	700
A <sub>1</sub> E <sub>2</sub> T <sub>1</sub>	450	850	2150	2600	2950	2400	A <sub>1</sub> E <sub>1</sub> T <sub>1</sub>	473	950	2750	2900	4300	2500
E <sub>2</sub> T <sub>2</sub>	470	1000	1450	1300	1050	1100	T <sub>2</sub> E <sub>1</sub>	493	2300	4500	3850	4400	3300
A <sub>3</sub> E <sub>3</sub>	602	800	660	390	420	270	A <sub>3</sub> E <sub>2</sub>	625	560	450	250	310	190
A <sub>1</sub> E <sub>3</sub> T <sub>2</sub>	622	310	390	790	610	640	A <sub>1</sub> E <sub>2</sub> T <sub>2</sub>	645	320	790	740	920	560
A <sub>2</sub> E <sub>3</sub> T <sub>1</sub>	642	150	700	640	800	600	A <sub>2</sub> E <sub>2</sub> T <sub>1</sub>	665	180	720	1030	1250	970
E <sub>3</sub> T <sub>3</sub>	662	170	240	200	160	170	E <sub>2</sub> T <sub>3</sub>	685	300	440	380	340	300
A <sub>4</sub> E <sub>4</sub>	774	320	220	110	100	70	A <sub>4</sub> E <sub>3</sub>	797	230	160	90	80	70
A <sub>3</sub> E <sub>4</sub> T <sub>1</sub>	794	130	280	210	240	190	A <sub>3</sub> E <sub>3</sub> T <sub>1</sub>	817	140	250	220	220	130
A <sub>2</sub> E <sub>4</sub> T <sub>2</sub>	814	70	170	240	220	220	A <sub>2</sub> E <sub>3</sub> T <sub>2</sub>	837	90	240	320	360	270
A <sub>1</sub> E <sub>4</sub> T <sub>3</sub>	834	40	90	110	100	100	A <sub>1</sub> E <sub>3</sub> T <sub>3</sub>	857	50	140	200	200	180
E <sub>4</sub> T <sub>4</sub>	854	40	40			30	E <sub>3</sub> T <sub>4</sub>	877	40	65	50	50	40
A <sub>5</sub> E <sub>5</sub>	946	140	80		30	20	A <sub>5</sub> E <sub>4</sub>	969	90	50		30	15
A <sub>4</sub> E <sub>5</sub> T <sub>1</sub>	966	60	100	85	80	50	A <sub>4</sub> E <sub>4</sub> T <sub>1</sub>	989	65	90	55	70	40
A <sub>3</sub> E <sub>5</sub> T <sub>2</sub>	986	25	70	100	90	80	A <sub>3</sub> E <sub>4</sub> T <sub>2</sub>	1009	35	100	120	115	85
A <sub>2</sub> E <sub>5</sub> T <sub>3</sub>	1006	15	35	60	50	60	A <sub>2</sub> E <sub>4</sub> T <sub>3</sub>	1029	20	60	90	80	75
A <sub>1</sub> E <sub>5</sub> T <sub>4</sub>	1026	15	25	25	15	10	A <sub>1</sub> E <sub>4</sub> T <sub>4</sub>	1049	10	30	35	25	40
E <sub>5</sub> T <sub>5</sub>	1046		10				E <sub>4</sub> T <sub>5</sub>	1069		10		10	10
A <sub>6</sub> E <sub>6</sub>	1118	80	36		16	10	A <sub>6</sub> E <sub>5</sub>	1141	55	25		15	12
A <sub>5</sub> E <sub>6</sub> T <sub>1</sub>	1138	35	49	37	33	17	A <sub>5</sub> E <sub>5</sub> T <sub>1</sub>	1161	40	45	26	24	17
A <sub>4</sub> E <sub>6</sub> T <sub>2</sub>	1158	16	30	44	35	37	A <sub>4</sub> E <sub>5</sub> T <sub>2</sub>	1181	15	48	45	45	35
A <sub>3</sub> E <sub>6</sub> T <sub>3</sub>	1178	10	23	33	30	31	A <sub>3</sub> E <sub>5</sub> T <sub>3</sub>	1201	10	32	45	46	34
A <sub>2</sub> E <sub>6</sub> T <sub>4</sub>	1198		13	20	12	15	A <sub>2</sub> E <sub>5</sub> T <sub>4</sub>	1221		21	25	24	27
A <sub>1</sub> E <sub>6</sub> T <sub>5</sub>	1218					8	A <sub>1</sub> E <sub>5</sub> T <sub>5</sub>	1241		10	13	10	10
A <sub>7</sub> E <sub>7</sub>	1290	40	14				A <sub>7</sub> E <sub>6</sub>	1313	26	12			
A <sub>6</sub> E <sub>7</sub> T <sub>1</sub>	1310	19	21	11			A <sub>6</sub> E <sub>6</sub> T <sub>1</sub>	1333	24	18	13		6
A <sub>5</sub> E <sub>7</sub> T <sub>2</sub>	1330	10	17	21		16	A <sub>5</sub> E <sub>6</sub> T <sub>2</sub>	1353	13	25	18		11
A <sub>4</sub> E <sub>7</sub> T <sub>3</sub>	1350	5	10	13		16	A <sub>4</sub> E <sub>6</sub> T <sub>3</sub>	1373	12	16	23		10
A <sub>3</sub> E <sub>7</sub> T <sub>4</sub>	1370		6	8		5	A <sub>3</sub> E <sub>6</sub> T <sub>4</sub>	1393	7	11	14		12
A <sub>2</sub> E <sub>7</sub> T <sub>5</sub>	1390			5		5	A <sub>2</sub> E <sub>6</sub> T <sub>5</sub>	1413			7		7
							A <sub>1</sub> E <sub>6</sub> T <sub>6</sub>	1433					4

<sup>a</sup> Composition of the aminolyzed products having one or two piperidine end groups (see Scheme I), in which A =  $-\text{CO}-(\text{CH}_2)_4-\text{CO}-$ , E =  $-\text{O}-(\text{CH}_2)_2-\text{O}-$ , and T =  $-\text{CO}-\text{Ph}-\text{CO}-$ . <sup>b</sup> The molecular ions of these products appear in the positive FAB mass spectra as  $(M + 1)^+$ .

is well above 90%, and this implies that the exchange reaction is practically over; i.e. the samples are pure copolymers.

However, from the data in Table III it is not possible to determine whether the copolymer number average block lengths,  $\langle n_{\text{EA}} \rangle$  and  $\langle n_{\text{ET}} \rangle$ , decreases steadily, as predicted on thermodynamic grounds. In fact, to compute  $\langle n_{\text{EA}} \rangle$  and  $\langle n_{\text{ET}} \rangle$  using eqs 7 and 8, we need additional information about the molecular weights and about the molar fraction of the homopolymers in the mixture.

In order to sort out the copolymer microstructure from the mass spectral data, the intensities of the peaks corresponding to homooligomers were excluded from the calculation and the reduced set of data was analyzed by the best-fitting approach. The MACO 4 computer program<sup>19</sup> (see Experimental Section) was employed to simulate the experimental data and to characterize the sequence distribution of the eight copolymers obtained by the melt-mixing process. In Table IV (column 2) we report the eight P-matrices (each made of four matrix elements) which yielded the lowest error level (AF) in the simulation process. The remaining columns of Table IV report the attributes of each P-matrix (evaluated using eqs 12 and 13): the associated copolymer composition, the associated extent of exchange, and the associated number average block length in the copolymer.

Curves in Figure 3 show the variation of the copolymer number average lengths,  $\langle n_{\text{EA}} \rangle$  and  $\langle n_{\text{ET}} \rangle$ , with the reaction time and indicate that the predicted initial formation of block copolymers actually occurs and that at longer reaction times a random distribution is approached. The curves exhibit two different regimes: in the first 30–60 min, block lengths (and especially  $\langle n_{\text{EA}} \rangle$ ) show a steep fall, and then they reach the asymptotic value  $\langle n_{\text{EA}} \rangle =$

$\langle n_{\text{ET}} \rangle = 2$  (which coincides with the predicted value for a 50:50 copolymer). This means that the formation of a rigorously random copolymer by the process in eqs 1 and 2 comes to completion in about 1 h. A similar behavior is also found by plotting the extent of exchange (EE) versus the reaction time (Figure 4). The curve exhibits a sharp increase of EE in the first hour, followed by a much slower growth, up to nearly 100%.

Figure 5 (curve a) shows the behavior of the copolymer composition as a function of time, which follows the same pattern found when the calculations were made using the data-partitioning method (Table III).

The excess of adipic units in the copolymer formed in the first stages of the melt-mixed reaction may be justified by the presence of the low molecular weight oligomers in the starting PEA sample. Thus, the copolymer can be formed by attack of the PEA oligomers on the PET macromolecules.

This hypothesis is valid if the composition of the low molecular weight cooligomers determined by FAB-MS data of the melt-mixed samples is representative of the whole system; all the computations are based on this supposition.

A confirmation of the proposed mechanism was obtained by analyzing the mass spectra of the aminolyzed melt-mixed P10, P30, P60, P120, and P270 samples (see Experimental Section). In fact, the aminolysis reduces the size of macromolecules, forming low molecular weight products<sup>16,17,26</sup> and, for these partially degraded materials, the differences between the "true" composition and the composition detected by MS becomes neglectable.

In Figure 6a,b the positive FAB mass spectra of the P20 and P270 samples are shown. Peaks corresponding to cyclic oligomers are very weak or absent. Instead, the



**Table VI**  
**Results of the Analysis on FAB-MS Spectra of the Aminolyzed PEA-PET Melt-Mixed Samples Using the Best-Fitting Approach**

sample	P-matrix <sup>a</sup>	$c_{EA}/c_{ET}^b$	EE <sup>c</sup>	$\langle n_{EA} \rangle^d$	$\langle n_{ET} \rangle^d$	AF <sup>e</sup>
P10	0.97/0.03/0.51/0.49	95/5	54	33.3	2.0	4.4
P30	0.86/0.14/0.50/0.50	78/22	64	7.1	2.0	8.8
P60	0.70/0.30/0.49/0.51	62/38	79	3.3	2.0	6.6
P120	0.53/0.47/0.63/0.37	52/48	90	2.1	1.6	6.0
P270	0.46/0.54/0.54/0.46	50/50	92	1.9	1.9	7.0

<sup>a</sup> First-order Markoffian P-matrix elements resulting from best-fit ( $P_{EA}/P_{EAET}/P_{ETEA}/P_{ETET}$ ). <sup>b</sup> Calculated copolymer composition (EA/ET molar ratio) using eq 12. <sup>c</sup> Calculated extent of exchange using eq 14. <sup>d</sup> Calculated number average lengths of EA and ET units in the copolymer by eq 13. <sup>e</sup> Agreement factor computed using eq 16.

most intense peaks correspond to two series of products having one or two piperidine end groups and different amounts of adipic and terephthalic units in the molecule (Table V).

Mass spectra simulation of the five positive FAB-MS spectra of the aminolyzed samples P10, P20, P60, P120, and P270 was performed using the program Maco 4. The outputs of the calculations are reported in Table VI. The best-fit P-matrices in Table VI show a reasonable agreement with the corresponding P-matrices for samples M10, M30, M60, M120, and M270 (Table IV). Thus, the decrease of the number average block lengths  $\langle n_{EA} \rangle$  and  $\langle n_{ET} \rangle$  at the initial stages of the process is extremely rapid and goes on until  $\langle n_{EA} \rangle$  and  $\langle n_{ET} \rangle$  approach the asymptotic value. The extent of exchange (EE) in Table VI increases with the reaction time. Also the composition of the copolymer formed (Table VI) varies as a function of the extent of exchange. Copolymer compositions derived from the aminolyzed samples (Figure 5, curve b) display some variations with respect to the corresponding data in Figure 5a; nevertheless, the time-dependence of the copolymer composition is the same. These results indicate that the attempt of deriving the overall copolymer composition from the analysis of low molecular weight species is justified since, in this case, the latter species actually reflect the overall sample.

## Conclusions

The work presented here focuses on the difficulties encountered in the direct analysis of the composition and microstructure of copolyesters formed in the melt-mixing reaction between two homopolyesters.

Because the <sup>1</sup>H NMR yields only dyad information (as is usually the case for copolyesters) and the presence of unconverted homopolymers in the mixture creates problems about the copolymer microstructure determination, only a very crude estimate of the copolymer composition can be obtained in these cases.

FAB-MS detects on the contrary oligomers up to octamers (providing therefore sufficient information) and represents an adequate analytical tool. The experiments and algorithms necessary to extract the relevant quantitative information from the mass spectral data were discussed in detail. The improved modeling capability allowed also testing of the mechanism operating in the exchange process. In fact, the copolymer composition was found to vary with the reaction time (Figure 5), and this was considered a diagnostic test in favor of the active chain end reaction of the low molecular weight oligomers of PEA on the PET macromolecules.

Furthermore, the reaction profile (i.e., the formation of block copolyesters in the initial stages of the exchange

reaction, Figure 3) has been established quantitatively for the first time.

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- In the present case, NMR spectroscopy does not distinguish between linear chains and cycles. This structural information is instead obtained by MS.

**Registry No.** PET, 25038-59-9; PEA, 24938-37-2; PEA (SRU), 24937-05-1; (adipic acid)(ethylene glycol)(terephthalic acid) (block copolymer), 142655-97-8.