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Kinetics and Mechanisms of Poly(poly(ethylene terephthalate)-*co*-poly-(ε-caprolactone)) Catalyzed Randomization: Influence of End Groups

Thomas Tanguy,[†] Jean-Pierre Bonnet,[†,§] Yaroslav V. Kudryavtsev,[‡] Martine Tessier,[†] and Alain Fradet*[,†]

[†]Université Pierre et Marie Curie-Paris6, Laboratoire de Chimie des Polymères, Courrier 184, 4 Place Jussieu, Paris France ; CNRS, UMR 7610, Paris, France, and [‡]Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, 29 Leninsky Prospekt, Moscow 119991, Russia. [§]Present address: Université de Picardie-Jules Verne, Laboratoire LRCS, UMR 6007, 33 Rue Saint-Leu, Amiens, France 80039.

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ABSTRACT: Hydroxy−ester interchanges were found to be the predominant reactions involved in poly(ethylene terephthalate)−poly(ε-caprolactone) copolyester randomization. Even for high molar-mass copolyesters having low hydroxyl end group concentration, kinetic studies show that ester−ester interchanges play a minor role. Reaction rate was almost proportional to hydroxyl end groups concentration. The randomization kinetics was studied by ^{1}H NMR on copolyesters obtained in situ by reacting a series of poly(ethylene terephthalate)s of various molar masses and end groups with ε-caprolactone, in the molten state and in the presence of $\mathrm{Ti(OBu)_4}$ catalyst. A mechanism involving parallel catalyzed second-order hydroxy−ester and ester−ester interchanges is proposed for the randomization step and perfectly fits experimental data. This study clearly shows that the nature and concentration of hydroxyl end groups must be carefully controlled for reliable synthesis of copolyesters by homopolyester melt blending.

Introduction

Almost all condensation polymers present reactive groups inside the chain (e.g., ester, amide, carbonate) or at chain ends (e.g., hydroxy, carboxy, amine) and may undergo interchange reactions when heated in the melt. Such reactions, e.g., ester−ester or amine−ester reactions, have been known and used for a long time to synthesize copolymers starting from homopolymer mixtures or blends.[1] It is well-known, for instance, that mixing homopolyesters in the melt rapidly results in the formation of block copolymers, which slowly randomize upon prolonged heating changing molar mass and chain segment distributions.[2] The same reactions make it difficult to introduce defined terminal groups or to introduce comonomers in a defined sequence. These processes also alter morphology significantly as random copolymers are less prone to crystallize. On the other hand, when transesterification-formed random copolyesters are annealed at temperature lower than the melting temperature of one of the homopolyesters, transesterification reactions can promote the formation of block copolyesters via crystallization induced sequential reordering.[3−11] In some applications, e.g., polymer functionalization or in situ compatibization of polymer blends, interchange reactions are highly welcome provided they are carefully controlled. One necessary condition to achieve this is a better understanding of the basic processes occurring in melts of polycondensates, therefore a better knowledge of interchange reaction kinetics.

A number of kinetic studies have been reported in the literature on ester interchange reactions. Two main types of reaction are put forward to explain the experimental results: ester−ester direct reactions and end group−ester reactions. Since condensation polymers always contain a non-negligible and often uncontrolled amount of end groups, the determination of the relative contribution of these two reactions in experimental conditions of polyester melt blending is of great practical interest.

Murano and Yamadera[12] studied ester interchange reactions taking place in poly(ethylene terephthalate)−poly(ethylene sebacate) (PET−PES) blends with residual $\mathrm{Zn(OAc)_2}$ and $\mathrm{Sb_2O_3}$ catalysts, showing that the reaction proceeds according to an a overall second-order mechanism. Three processes can be involved:[12]

Chain growth

$$\begin{aligned}&\cdots-\mathrm{T{-}E{-}OH}+\cdots-\mathrm{S{-}E{-}OH}\\ &\rightleftarrows\cdots-\mathrm{T{-}E{-}S}-\cdots+\mathrm{HO{-}E{-}OH}\end{aligned}\qquad\text{(i)}$$

Direct ester−ester reaction

$$\begin{aligned}&\cdots-\mathrm{T{-}E{-}T{-}E}-\cdots+\cdots-\mathrm{S{-}E{-}S{-}E}-\cdots\\ &\rightleftarrows\cdots-\mathrm{T{-}E{-}S{-}E}-\cdots+\cdots-\mathrm{S{-}E{-}T{-}E}-\cdots\end{aligned}\qquad\text{(ii)}$$

Hydroxy−ester reaction:

$$\begin{aligned}&\cdots-\mathrm{T{-}E{-}OH}+\cdots-\mathrm{S{-}E{-}S{-}E}-\cdots\\ &\rightleftarrows\cdots-\mathrm{T{-}E{-}S{-}E}-\cdots+\cdots-\mathrm{S{-}E{-}OH}\\ &\cdots-\mathrm{S{-}E{-}OH}+\cdots-\mathrm{T{-}E{-}T{-}E}-\cdots\\ &\rightleftarrows\cdots-\mathrm{S{-}E{-}T{-}E}-\cdots+\cdots-\mathrm{T{-}E{-}OH}\end{aligned}\qquad\text{(iii)}$$

where S, T, and E represent sebacoyl, terephthaloyl, and 2-oxyethoxy moieties, respectively.

Since OH group concentration is usually small (high molar mass polymers) and interchange reactions are carried out at atmospheric pressure, which do not favor ethylene glycol elimination, the contribution of reaction i to the randomization process is not predominant. If the hydroxy groups of PET and PES have same reactivity, the sum of the two equations of system

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*To whom correspondence should be addressed. alain.fradet@upmc.fr.

iii can obviously be written as reaction ii. The contribution of OH end groups is consequently hidden in the overall process and it is not possible to determine the relative contribution of hydroxy–ester interchange and direct ester–ester interchange, unless the influence of OH concentration on the overall process is specifically studied.

If the contribution of hydroxy–ester groups is predominant, small and uncontrolled variations of OH group content would result in large variations of randomization rate upon polyester blending and, therefore, of resulting blend properties.

Devaux et al. studied the relative contribution of hydroxy–ester versus ester–ester reactions in the randomization of bisphenol A polycarbonate– (PC–) poly(butylene terephthalate) (PBT) blends and of PC–PET blends using model reactions and pointed out the high rate of ester–ester interchanges with respect to the OH–ester and OH–carbonate interchanges.[13−15] However, this case is very specific since phenol end groups do not react with ester groups. The first alcohol–carbonate interchange results in the formation of unreactive phenol end groups, therefore to the formation of a phenol-terminated copolymer in which only ester–carbonate interchange can take place. The important role of residual tetrabutoxytitanium catalyst present in starting PBT and PET was also underlined in these studies.[14,15] Montaudo et al.[16] also came to the conclusions that ester-carbonate reaction predominates when studying interchange reactions in PC–PBT blends using end-capped PBT or PBT of various molecular weight and end group content. However, the carbonate–ester reaction cannot really be compared to ester–ester blends due to the low reactivity of phenol end groups. The kinetics of ester-interchange reactions taking place between end-capped aliphatic oligoesters was studied by Ramjit et al.[17−19] by means of mass spectrometry. The kinetic model involved a second-order direct ester–ester interchange mechanism. However, due to the harsh reactions conditions used (several hours at 312 °C), degradation reactions are very likely in this case. A second-order direct ester–ester reaction mechanism was also postulated for PET–poly(ethylene naphthalate) (PEN) melt reactions on the basis of studies carried out on either model[20] and polymeric[21−26] systems, for poly(ethylene terephthalate-*co*-4-oxybenzoyl)–PET blends[27,28] and for various aromatic and aliphatic–aromatic polyester blends.[29,30] In these studies of polyester blending, the influence of end groups was not investigated. The influence of end groups in PET–PBT reaction was studied by Backson et al. using neutron scattering on PET of various molar masses.[31] No significant difference was found between the various polyesters and the authors concluded that ester–ester interchanges are predominant. On the other hand, the great importance of hydroxy–ester reactions in PET–PEN melt blending was pointed out by Kenwright et al.[32] and Collins et al. in a series of articles.[26,33,34] The second-order rate constant was divided by three when the contribution of OH end groups was removed by capping with trifluoroacetic anhydride. The contribution of COOH end groups was also found negligible in these studies. Krentsel et al.[35] reported the same rate constants for a melt of commercial PET and PEN ($M_\eta \approx 10^4$) containing residual catalyst and that of catalyst-free synthesized PET and PEN ($M_\eta \approx 10^3$), the greater amount of reactive end groups compensating the absence of catalyst in the latter case.

This short survey shows that there is no complete agreement about the relative importance of ester–ester and hydroxy–ester interchange reactions, i.e., the influence of the nature and concentration of polymer end groups on ester interchange processes. These discrepancies may arise from the use of polymers having different initial miscibility or, in some studies, from the use of industrial polymers, in which the nature and concentration of end groups and the presence of residual catalyst were not taken into account.

In a previous work,[36] we reported the synthesis of PET/poly(lactone) copolyesters by the bulk reaction of high-molar-mass PET with lactones, such as ε-caprolactone (CL) and δ-valerolactone (VL). The reaction was carried out at 240–270 °C in the presence of tetrabutoxytitanium as catalyst and led very rapidly to high molar mass copolyesters. A series of PET–poly(ε-caprolactone) copolyesters (PET–PCL) with various terephthaloyl/lactone mol ratios were prepared and characterized. Their degree of randomness, *B*, determined by ^{1}H NMR, was < 1, which indicated that they still presented some block copolymer character after 2 h of reaction.

The PET–ε-caprolactone system appears quite suited to the study of ester interchange reactions: The initial reaction medium is not an immiscible polymer blend, but a miscible polymer–monomer mixture. When the medium is heated to reaction temperature, CL ring-opening polymerization and ester interchange reactions take place simultaneously, leading to the formation of a block copolymer. MALDI–TOF MS studies of reaction medium at reaction times as short as 2 min showed the absence of homopolymer chains, a strong indication of the homogeneous nature of reaction medium from the very beginning of reaction.[36] In these conditions, ester interchanges are not disturbed by polymer immiscibilty problems, which would hinder or slow down randomization during the first steps of reaction.

In this paper, we report a kinetic study of ester interchange reactions taking place in PET–ε-caprolactone copolyesters. In order to obtain insights on reaction mechanism and on the influence of the nature and content of end groups, the reactions were carried out on commercial high-molar-mass PET, on hydroxy-terminated-PET of various molar-masses and on methylester- and carboxy-terminated PET oligomers. Controlled amounts of $Ti(OBu)_4$ were used to catalyze the reaction and the variations of triad mole ratios versus time were followed by ^{1}H NMR.

Experimental Section

Materials. Ethylene glycol and dimethyl terephthalate (99% Acros Organics), bis(2-hydroxyethyl) terephthalate, ε-caprolactone, and tetrabutoxytitanium (99% Aldrich Co) were used as received. Poly(ethylene terephthalate) (Aldrich Co) was powdered by cryogenic crushing and vacuum-dried overnight at 100 °C before use ($\overline{M_w}$ = 45800 from inherent viscosities measurements in 1/1 (v/v) phenol/*o*-dichlorobenzene at 25 °C), using the molar mass viscosity relationship given in ref 37). This polymer contained 82 ppm of Sb from Sb_2O_3 catalyst.

Syntheses. *α,ω-Dimethylester Poly(ethylene terephthalate) (P6).* First, 62 g (1 mol) of ethylene glycol and 388 g (2 mol) of dimethyl terephthalate were placed in a 500 mL glass reactor equipped with a central mechanical stirrer, a nitrogen inlet, a distillation head connected to a condenser, and a receiver flask. The reactor was placed in a salt bath at 185 °C. When the mixture was molten, 3.03 mL of a $Ti(OBu)_4$ solution in CH_2Cl_2 (10 wt %) was introduced into the mixture with the help of a hypodermic syringe. Bath temperature was raised gradually to 195 °C and methanol distilled off. After 2 h heating at this temperature, pressure was slowly reduced to 0.1 mbar and temperature was raised to 280 °C (2 h). The excess of dimethyl terephthalate was removed by distillation. During this stage, the condenser was heated to prevent clogging due to the condensation of some dimethyl terephthalate.

α,ω-Dihydroxy Poly(ethylene terephthalate) (P1–P4). First, 50 g (0.2 mol) of bis(2-hydroxyethyl) terephthalate were placed in a 100 mL glass reactor equipped with a central mechanical stirrer, a nitrogen inlet, a distillation head connected to a condenser and a receiver flask. The reactor was placed in a salt bath at 280 °C and pressure was reduced to 0.1 mbar for 1,2-ethanediol distillation. The reaction took 24 h for P4, 6 h for P3, 4 h for P2, and only 2 h for P1.

α,ω-Dicarboxy Poly(ethylene terephthalate) (P7). Here, 40 g (0.16 mol) of bis(2-hydroxyethyl) terephthalate and 31,4 g (0.19 mol) of terephthalic acid were heated at 320 °C under atmospheric pressure for 6 h and then at 0.1 mbar for another 6 h.

Kinetic Studies. The general procedure is described below with an example (50/50 mass PET−PCL copolyester): PET (2.5 g) and ε-caprolactone (2.5 g) were placed in a 50 mL glass reactor equipped with nitrogen inlet and outlet and a central mechanical stirrer. The reactor was placed in a salt bath at 240 °C. The reaction medium became rapidly homogeneous, and after 5 min of heating, its temperature was 240 °C. For reactions carried out with added catalyst, 200 μL of a $Ti(OBu)_4$ solution (125 mg $Ti(OBu)_4$ in 5 mL of CH_2Cl_2) were introduced into the medium with the help of a hypodermic syringe. This time was taken as the initial reaction time ($t = 0$) in kinetic studies. Samples were then taken during the reaction at predetermined time intervals for ^{1}H NMR determination of the molar fractions of TET, TEL and LEL triads. The time at which CL polymerization was complete (conversion >99.5%) was taken as time $t = t_0$ in the randomization kinetic study. Since some CL vaporization was noticed between $t = 0$ and $t = t_0$, the actual 6-oxyhexanoyl units (L units) content in PET−PCL copolyesters was determined by ^{1}H NMR. Initial concentrations in catalyst and OH groups were also corrected from the corresponding reaction medium mass loss.

Determination of Rate Constants. The experimental values of the degree of randomness *B*, calculated from triad molar fractions, were fitted to the theoretical rate equation system (eq 3 and 10) using built-in numerical differential equation system solving and nonlinear optimization routines of Mathematica 7 (Wolfram Co.). Correlation coefficients and standard error on rate constants estimates were calculated for each fitted system.

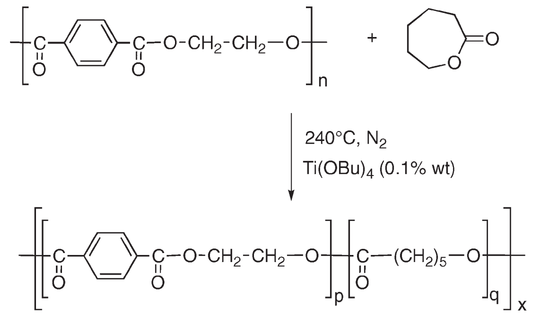
Measurements. *^{1}H NMR spectra* were recorded on a Bruker Avance 500 spectrometer. Samples were dissolved in $CDCl_3$/trifluoroacetic acid solvent mixture (4/1 v/v), and spectra were recorded immediately to avoid end group esterification by trifluoroacetic acid (TFA). Chemical shifts were referenced to residual $CHCl_3$ at 7.26 ppm.

Size exclusion chromatography (SEC) was performed with an equipment comprising a Rheodyne injector, a Waters 515 pump, a Waters 410 differential refractometer, an Ultrastyragel column set (19 mm ×300 mm, 500 + 10^3 + 10^4 Å), and a Waters Millenium software. Tetrahydrofuran (5 mL/min) was used as eluent. Calibration was carried out by SEC−MALDI−TOF MS off-line coupling:[36] 200 μL of a polymer solution in THF (40 $g \cdot L^{-1}$) was injected and polymer fractions were collected every 15 s (1.25 mL) using a Waters fraction collector. The molar masses of these fractions were determined by MALDI−TOF MS. Selected fractions were then used to calibrate the system.

MALDI−TOF mass spectrometry was performed using a PerSeptive Biosystems Voyager Elite time-of-flight mass spectrometer equipped with a nitrogen laser (λ = 337 nm). Spectra were recorded in a reflector or linear delayed extraction mode at an acceleration voltage of 25 kV. The matrices, α-cyano-4-hydroxycinnamic acid (HCCA) or 2-(4-hydroxyphenylazo) benzoic acid (HABA) were dissolved in THF (20 $g \cdot L^{-1}$). NaI was added for control experiments (0.1 $g \cdot L^{-1}$). The SEC polymer fractions were evaporated to dryness and diluted with 50 μL of THF (2−5 $g \cdot L^{-1}$). A 5 μL aliquot of the polymer solution was mixed with 50 μL of the matrix solution. Then a 1 μL portion of the final solution was deposited onto the stainless steel sample slide and allowed to dry in air at room temperature. The MALDI−TOF mass spectra represent averages of 256 consecutive laser shots. For SEC calibration, the molar masses fractionated samples were taken at the peak maximum of smoothed spectra.

PET End Group Concentration. Hydroxyl end group content was determined by ^{1}H NMR. Carboxyl end group content was determined by titration following a procedure modified from refs 38 and 39. An accurately weighed PET sample of about 500 mg and 15 mL aniline were heated to 130 °C until complete dissolution in a round-bottomed flask fitted with a reflux condenser. This took approximately 10 min. After cooling down to 70 °C, 15 mL of chloroform was added through the reflux condenser, and the reaction medium was then rapidly cooled to room temperature in a water bath. Then 20 mL of solution was withdrawn and titrated with a 5 × 10^{-3} M solution of KOH in ethanol in the presence of bromothymol blue as indicator.

Scheme 1. Reaction between PET and ε-Caprolactone



Differential scanning calorimetry (DSC) were carried out on a DSC 2920-Modulated TA Instruments apparatus equipped with liquid nitrogen cooling accessory, at cooling and heating rates of 20 °C/min under nitrogen. Transition temperatures were measured on the second heating curves. Melting temperatures (T_m) were taken at the minima of the melting endotherms and glass transition temperatures (T_g) at the inflection point.

Results and Discussion

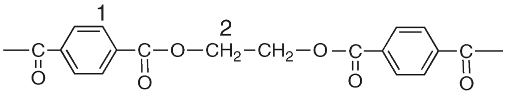
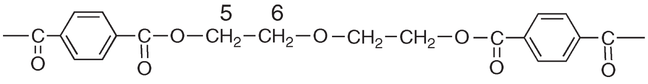
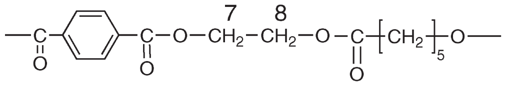
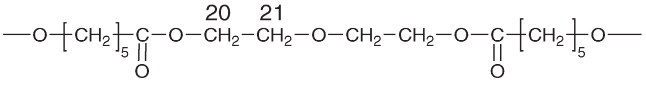
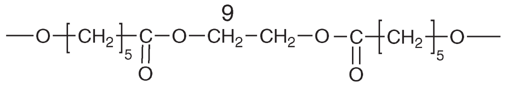
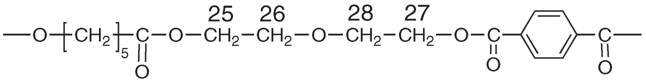
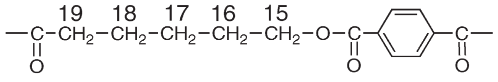
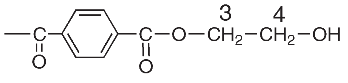
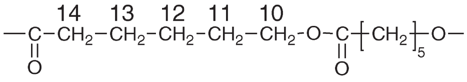
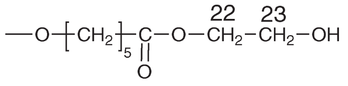
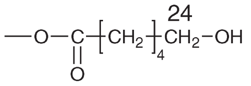
The reaction between poly(ethylene terephthalate) (PET) and ε-caprolactone (CL) (50/50 wt. mixture) was carried out at 240 °C for 210 min in the bulk, in the presence of tetrabutoxytitane ($Ti(OBu)_4$) as catalyst (0.1 wt %) (Scheme 1).

PET and CL are completely miscible at reaction temperature and the homogenization step was very short, leading to a molten reaction mixture. The reaction itself can be described as a very fast ring-opening polymerization (ROP) of CL immediately followed by ester interchange reactions, leading to the formation of a block copolyester, which slowly randomizes upon prolonged heating. Metal alkoxides, such as $Ti(OBu)_4$, are known to catalyze lactone ring-opening polymerizations as well as ester interchange reactions.[40] Only traces of free CL were detected in the copolyesters after 5 to 15 min reaction, while, in the absence of a catalyst, free CL was detected in reaction medium even after 60 min at 240 °C. The insertion of 6-oxyhexanoyl units in PET chains by interchange reactions leads to modifications in copolymer microstructure, reflected in the ^{1}H NMR spectra by the formation of new peaks assigned to LT dyads and to new E-centered triads, TEL and LEL, where T, E, and L represent terephthaloyl, 2-oxyethoxy, and 6-oxyhexanoyl units, respectively (Table 1).

The mol fraction of TET triads, which initially compose PET, decreases due to the formation of TEL and LEL triads. The variations with time of the mol fractions of the E-centered triads give information on randomization and ester exchange reaction kinetics and mechanisms.

Starting PETs. In order to study the influence of the nature and concentration of end groups on randomization kinetics, a series of PET with −COOH, −COOMe, and −OH end groups were synthesized. Hydroxy-terminated PETs were obtained by high temperature polycondensation of bis(2-hydroxyethyl)terephthalate under vacuum with elimination of 1,2-ethanediol, without the addition of any catalyst. PETs P1−P4, of various molar masses and OH content, were obtained by varying reaction time (Table 2). Carboxy-terminated P7 was obtained by reacting bis(2-hydroxyethyl)-terephthalate with excess terephthalic acid without catalyst

Table 1. Dyads and Triads Present in PET−PCL Copolyesters and Atom Numbering for ^{1}H NMR Assignments

E-centered Triads	Ether moieties
TET  	
TEL  	
LEL  	
Dyads	**Hydroxy end groups**
LT  	
LL  	
	

in similar conditions. Methylester-terminated P6 was synthesized from 1,2-ethanediol and excess dimethyl terephthalate. In this case, the addition of a catalyst (Ti(OBu)$_4$) was required to obtain a polymer. The amount of residual catalyst was, therefore, taken into account in the subsequent kinetic analysis. A commercial PET (P5), was also investigated in these studies. All polymers contained some carboxylic acid end groups (24−50 mmol/kg) arising from the well-known PET chain scission with formation of carboxylic acid end groups and acetaldehyde.[41,42] The thermal properties of these polymers are also reported in Table 2.

Structure and Sequential Composition of PET−PCL Copolyesters. The ^{1}H NMR spectrum of a PET−PCL copolyester obtained after 10 min reaction at 240 °C between low-molar-mass PET P1 and CL (50/50 wt %) is given in Figure 1.

In order to get information on the resonances of the hydroxy end groups and ether moieties formed by etherification side-reactions,[43,44] the spectra were assigned (Table 1) with the help of a 2D ^{1}H−^{1}H COSY 45 NMR experiment. The fractions of the three E-centered triads (TET, TEL or LET, and LEL) can be calculated from the relative integrations of the corresponding ^{1}H NMR resonances (H^2, H^8, and H^9, respectively[36]). H^9 resonance overlaps with the resonances arising from LT dyads (H^{15}), ether units (H^{20} and H^{25}), and LE−OH end groups (H^{22}). However, H^9 integration (I_9) can be calculated from H^{16}, H^{21}, H^{23}, and H^{26} integrations, since $I_{15} = I_{16}$, $I_{20} = I_{21}$, $I_{22} = I_{23}$, and $I_{25} = I_{26}$. The calculations were easier in the case of the −COOCH$_3$- and −COOH-terminated copolyesters obtained by reaction of ε-caprolactone with P6 and P7, respectively, since no ether units nor hydroxy end groups are present in these polymers.

The degree of randomness, B, which characterizes the extent of randomization in condensation copolymers, was derived in PET−PCL copolyesters from the value of triad molar fractions according to eq 1[36,45]

$$B = \left[1 - \left(f_{TET} + \frac{f_{TEL}}{2}\right)\right] \frac{2T + L}{L} \tag{1}$$

or

$$B = [1 - f_{ET}] \frac{2T + L}{L} \tag{2}$$

where f_{TET} and f_{TEL} are the mol fractions of TET and TEL + LET triads, T and L the mol fractions of T and L units and f_{ET} the mol fraction of ET dyads, respectively. Since some CL loss takes place during the very beginning of reaction, before CL polymerization is complete, the exact L-unit content in copolyesters was determined from the integration of the methylene resonances H^{14} and H^{19} of 6-oxyhexanoyl

Table 2. End Group Concentrations, Number-Average Molar Mass ($\overline{M_n}$), Glass Transition Temperature (T_g), Melting Temperature (T_m) and Melting Enthalpy (ΔH_m) of Starting PETs P1−P7

sample	[OH][a] (mmol·kg^{-1})	[COOH][b] (mmol·kg^{-1})	[COOMe][a] (mmol·kg^{-1})	$\overline{M_n}$[c] (g mol^{-1})	T_g (°C)	T_m (°C)	ΔH_m (J/g)
P1	667.3	32.0		2860	48	238	48
P2	251.7	42.0		6810	74	251	46
P3	157.0	24.7		11 010	77	246	36
P4	63.2	22.9		23 230	70	231	30
P5[d]	44.0	50.3		21 210	82	252	43
P6	0	24.0	2275	870		216	77
P7	0	263.2		7600	73	259	47

[a] Determined by ^{1}H NMR. [b] Determined by acid−base titration. [c] From end group content. [d] Commercial PET.

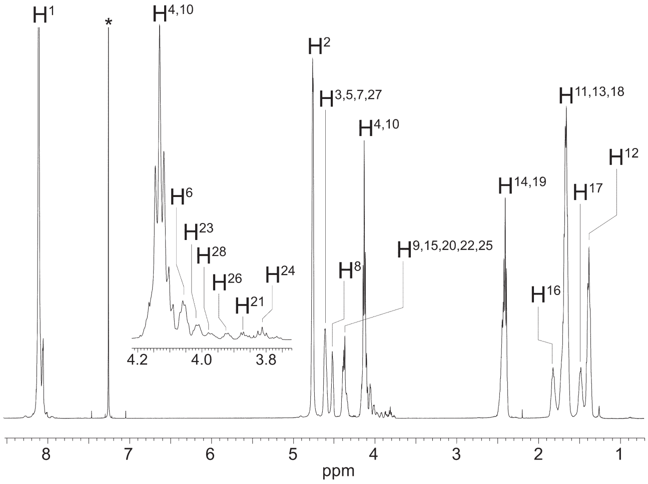


Figure 1. ^{1}H NMR spectrum of P1-PCL copolymer (50/50 wt) for a reaction time of 10 min at 240 °C (500 MHz, $CDCl_3$ + TFA, $\delta(CHCl_3)$ = 7.26 ppm).

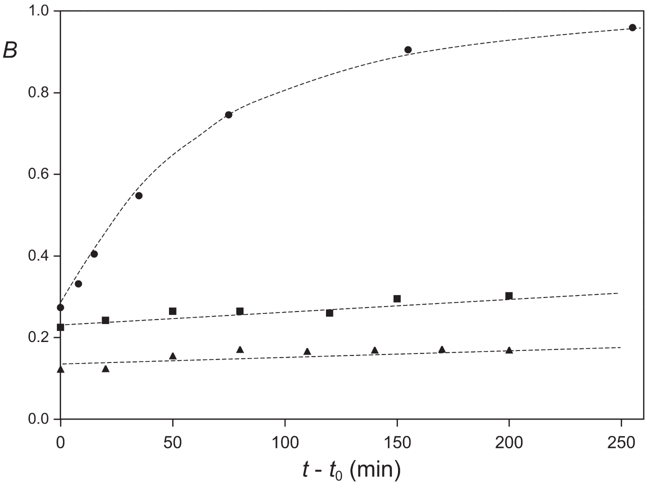


Figure 2. Variations of the degree of randomness, *B*, with time during the Ti-catalyzed randomization reaction of P7-PCL (COOH end groups) (▲), P6-PCL (COOMe end groups) (■), and P2-PCL (OH end groups) (●). Dashed curves are drawn only to better visualize B variations.

Scheme 2. Formation of Ti Carboxylates by Reaction between Carboxylic Acid and Tetrabutoxytitanium

units. In the kinetic study, the time corresponding to the first sample with a free CL amount lower than 0.5% was taken as time $t = t_0$.

Influence of the Nature of PET End Groups on Randomization Rate. The insertion of L units in PET chains was detected in the ^{1}H NMR spectra of the reaction products of CL with all studied PETs. However, ester interchange reaction rate strongly depends on the nature of end groups, as depicted in Figure 2.

A nearly random copolyester ($B > 0.9$) was obtained in about 180 min with hydroxy-terminated P2, while the variations of *B* were extremely slow in the case of COOMe-terminated P6 and even slower for carboxy-terminated P7. Copolyester randomization can proceed via interchanges between chain ester groups and via interchanges between end groups and chain ester groups. Since ester concentration is similar in each system, the contribution of interchanges between ester groups should be nearly the same in each case. The comparison of P6-PCL (COOMe end groups) and P2-PCL (OH end groups) curves of Figure 2 clearly shows that OH-ester interchanges are much faster than ester−ester or COOMe−ester interchanges. Therefore, as pointed out by some other authors,[26,32−34] the presence of hydroxy end groups plays a major role in copolyester randomization. The extremely slow rate of interchange reactions involving carboxy end groups is more surprising. This can be explained by the formation of titanium carboxylate groups as observed in Ti alkoxide-catalyzed OH+COOH direct esterifications (Scheme 2).[46,47] Ti carboxylates can react with hydroxy end groups to form ester groups and Ti−OH bonds, then new Ti alkoxide catalytic sites.[48] However, in the case of P7, no OH groups are present and the very low randomization rates indicates that, once formed, carboxylates cannot be displaced by other carboxylic acid groups nor by ester groups, thus blocking catalyzed interchange reactions.

Evolution of Copolyester Molar Mass during Randomization Reaction. The SEC chromatograms of samples withdrawn from the P1-PCL reaction medium at various reaction times are given in Figure 3.

An evolution toward higher molar masses, therefore a decrease of OH end group concentration, is observed during the reaction. This can be assigned to hydroxy−ester interchanges between chain ends with elimination of 1, 2-ethanediol (Scheme 3). This reaction is also involved in the last step of industrial PET syntheses starting from dimethyl terephthalate and excess 1,2-ethanediol. Etherification side reactions may also take place in these conditions, leading to MW increase.[43,44] However, even though a small amount of ether groups is present in all PET, this amount did not increase significantly during the randomization step and etherification reaction are not responsible for the MW increase.

Since randomization rate strongly depends on OH end group concentration ([OH]), it is necessary to know their variations with time in order to study randomization kinetics. [OH] could no longer be determined by NMR, due to peak overlapping with peaks relative to L units. However, total end group concentrations were obtained from the value

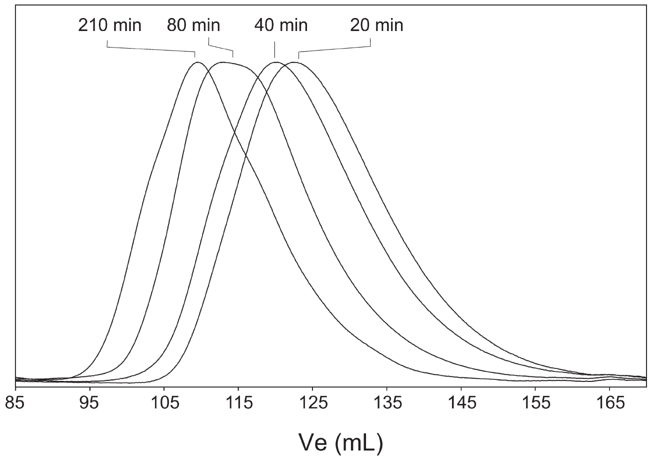
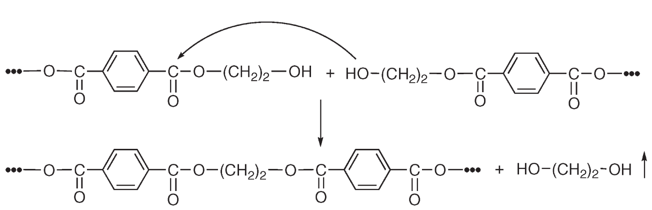


Figure 3. SEC chromatograms of P1-PCL copolyester at various reaction times (t-t_0).

Scheme 3. Growth of PET Chains via Hydroxy−Ester Interchange Reaction with Elimination of 1,2-Ethanediol



of the absolute number-average molar masses of these samples determined by off-line SEC/MALDI−TOF MS coupling: The samples were fractionated into narrow molar mass fractions. The molar masses of these narrow fractions were then measured by MALDI−TOF MS and the values obtained were used to "self-calibrate" starting SEC curves.[36] COOH end groups were determined by titration and found to slightly increase during the reaction (20 to 31 mmol/kg). Since no other types of end group are present, [OH] were calculated as being the difference between total end group and [COOH]. The variations of [OH] with time were fitted to a second-order rate equation:

$$-\frac{\mathrm{d[OH]}}{\mathrm{d}t} = k'[\mathrm{OH}]^2 \quad \text{or} \quad \frac{1}{[\mathrm{OH}]} - \frac{1}{[\mathrm{OH}]_0} = k't \qquad (3)$$

where k' is the rate constant and time $t = 0$ the time of catalyst introduction. The variation of $1/[\mathrm{OH}]$ - $1/[\mathrm{OH}]_0$ versus time (Figure 4) are linear, showing that OH group consumption is well modeled by a second-order rate equation. Rate constant k' was found equal to 0.042 kg mol^{-1} min^{-1} at 240 °C. This rate equation was included in the randomization kinetic analysis, to take into account [OH] variations.

Kinetic Analysis of PET−PCL Randomization. The variations of B with time were followed at 240 °C during the randomization step of copolyesters P1-PCL to P5-PCL. A mechanism involving parallel OH−ester and ester−ester interchange reactions was found to be consistent with experimental data. Because of the very low randomization rate observed for the system with high COOH concentration (P7-PCL) the contribution of COOH end groups in the randomization of P1−P5−PCL, which contain a very low amount of residual COOH, was neglected. The mechanism consists of 5 elementary reactions (Scheme 4).

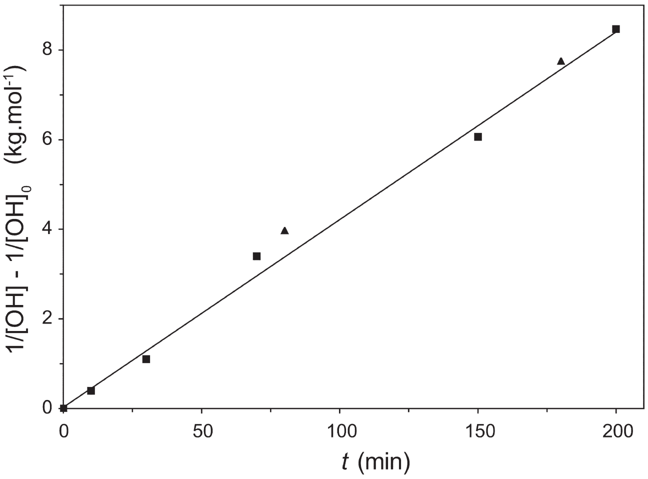


Figure 4. Plot of $1/[\mathrm{OH}] - 1/[\mathrm{OH}]_0$ as a function of time during P1-PCL (■) and P2-PCL (▲) randomizations.

(i) Reaction a corresponds to the ring-opening polymerization of CL via the well-established coordination−insertion mechanism in the presence of $\mathrm{Ti(OBu)_4}$ as initiator.[49] This step is nonlimiting since only traces of free CL monomer were experimentally found in copolyesters after 5 to 15 min of reaction, well before complete copolyester randomization. The initiation step leads to the formation of butylester-terminated PCL chains

(ii) Alkoxytitanium-terminated PCL chains (LOTi) formed through reaction a or residual butoxytitanium groups of starting catalyst can react with the ester functions of poly(ethylene terephthalate) via a mechanism essentially similar to the coordination−insertion mechanism (reaction b). ET dyads are replaced in PET main chain by LT dyads and EOTi groups are formed. EOTi can further react with LL dyads of PCL chains or blocks (reaction b′), forming EL dyads and LOTi groups. Both reactions lead to chain randomization.

(iii) It is well-known[46] that rapid exchange reactions take place between OH and titanium alkoxides. Such exchanges between OH end groups of PET (EOH) and LOTi moieties yield EOTi moieties and OH-terminated segments of PCL (reaction c). Apart from COOH end groups, which are not taken into account in the kinetic model, after a few minutes the reaction medium contains 4 types of chain ends, EOTi, LOTi, EOH and LOH, which are in equilibrium via reaction (c).

(iv) Finally, hydroxy−ester interchange reactions may take place between OH end groups (EOH or LOH) and Ti-coordinated ester groups (reaction d, rate constants k_2 and k_{-2}).

In the absence of OH groups, randomization is only due to reactions b and b′. With the assumption of equal rate constants, the sum of reactions b and b′ corresponds to $\mathrm{ET} + \mathrm{LL} \rightleftharpoons \mathrm{LT} + \mathrm{EL}$, i.e., to alkoxytitanium-catalyzed ester−ester interchange reaction. Both ester−ester interchange (reaction b + b′) and hydroxy−ester interchange (reaction d) change sequence lengths via an essentially entropy-driven process. Even though reactions between EOH end groups and ET dyads (or between LOH end groups and LL dyads) can occur, these have no influence on randomization kinetics since no new dyads or triads appear in these reactions. According to Scheme 4 and assuming second-order

Scheme 4. Mechanism Proposed for Alkoxytitanium-Catalyzed PET−PCL Randomization

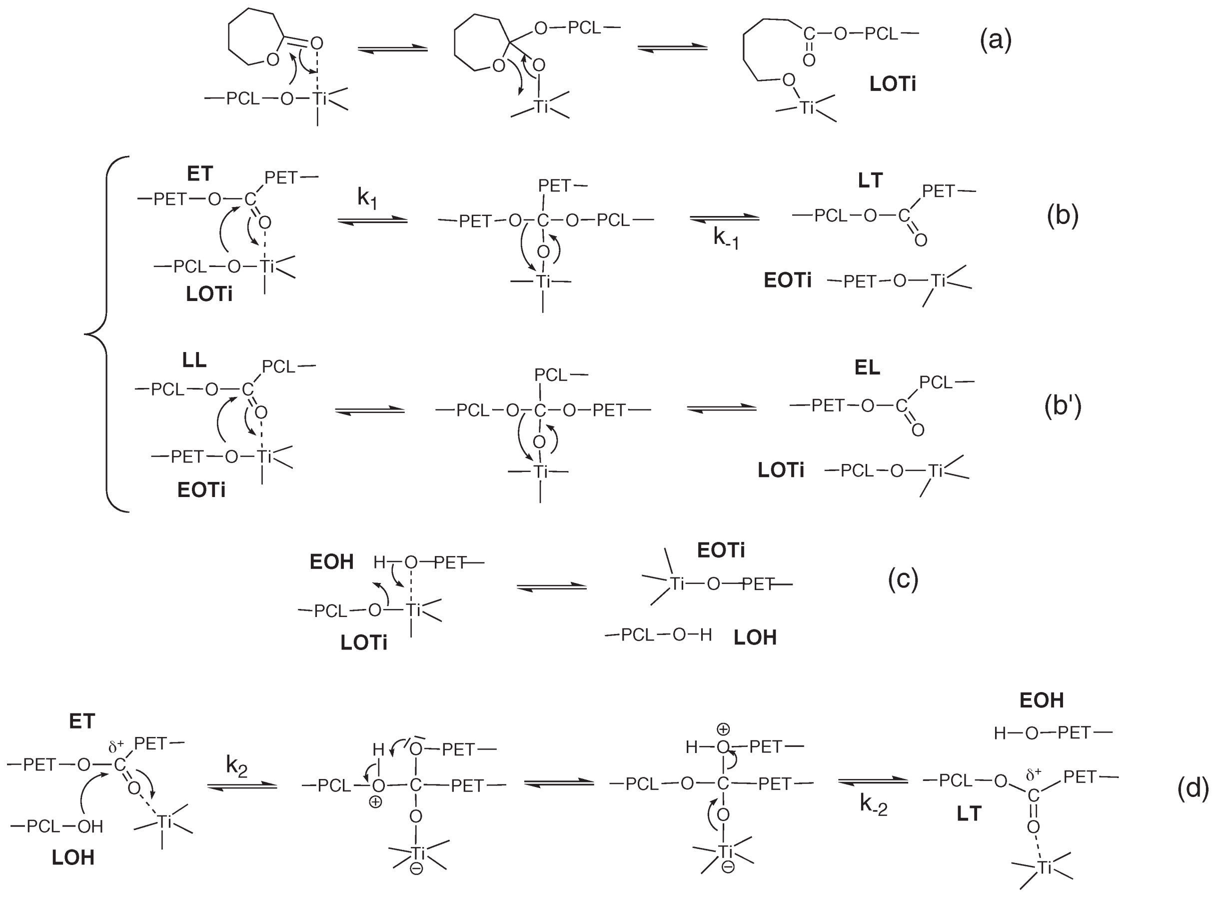


Table 3. Nonlinear Fit of the Variations of the Experimental Values of the Degree of Randomness, *B*, to Kinetic eqs 3 and 10 with Estimates of Rate Constants k_1 and k_2, Estimates of Standard Errors Δk_1 and Δk_2 on Rate Constants, and Values of the Adjusted Coefficient of Determination R^2

copolyester	k_1 (kg mol^{-1} min^{-1})	Δk_1 (kg mol^{-1} min^{-1})	k_2 (kg^2 mol^{-2} min^{-1})	Δk_2 (kg^2 mol^{-2} min^{-1})	R^2
P1-CL	0.019[a]		7.78	0.82	0.998
P2-CL	0.019[a]		7.98	0.43	0.999
P3-CL	0.019[a]		7.87	0.60	0.996
P4-CL	0.019[a]		7.09	0.83	0.997
P5-CL	0.019[a]		8.10	0.37	0.996
P7-CL	0.019	0.002			0.999

[a] Value obtained from P7.

reactions, the generation rate of ET dyads can be written as follows:

$$\frac{\mathrm{d}[\mathrm{ET}]}{\mathrm{d}t} = k_{-1}[\mathrm{LT}][\mathrm{EOTi}] - k_1[\mathrm{ET}][\mathrm{LOTi}] + k_{-2}[\mathrm{LT}][\mathrm{EOH}][\mathrm{cata}]_0 - k_2[\mathrm{ET}][\mathrm{LOH}][\mathrm{cata}]_0 \qquad (4)$$

where $[\mathrm{cata}]_0$ is the initial Bu−O−Ti group concentration. Some additional hypotheses are made:

(i) The contributions of noncatalyzed reactions are negligible. This is reasonable as ester-terminated PET could not be synthesized without catalyst.

(ii) Direct and reverse reactions have the same rate constants, i.e., $k_1 = k_{-1}$ and $k_2 = k_{-2}$. This is reasonable considering the quite similar nature of reactants and reaction products in interchange reactions.

(iii) The principle of equal reactivity is fulfilled by OH groups and by −R−O−Ti groups, meaning that at any time, but a short transitional step at the beginning of reaction, the ratio of EOH to LOH concentrations and the ratio of EOTi to LOTi concentrations are constant and equal to the

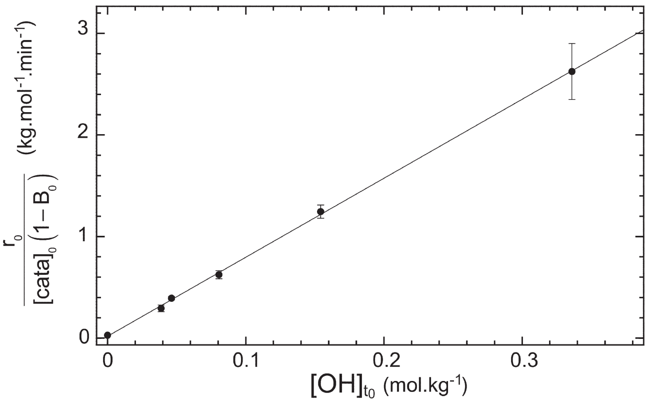


Figure 5. Plot of initial reaction rate r_0, corrected from catalyst concentration and initial randomization state, against hydroxy end group concentration at t_0, $[\mathrm{OH}]_{t_0}$.

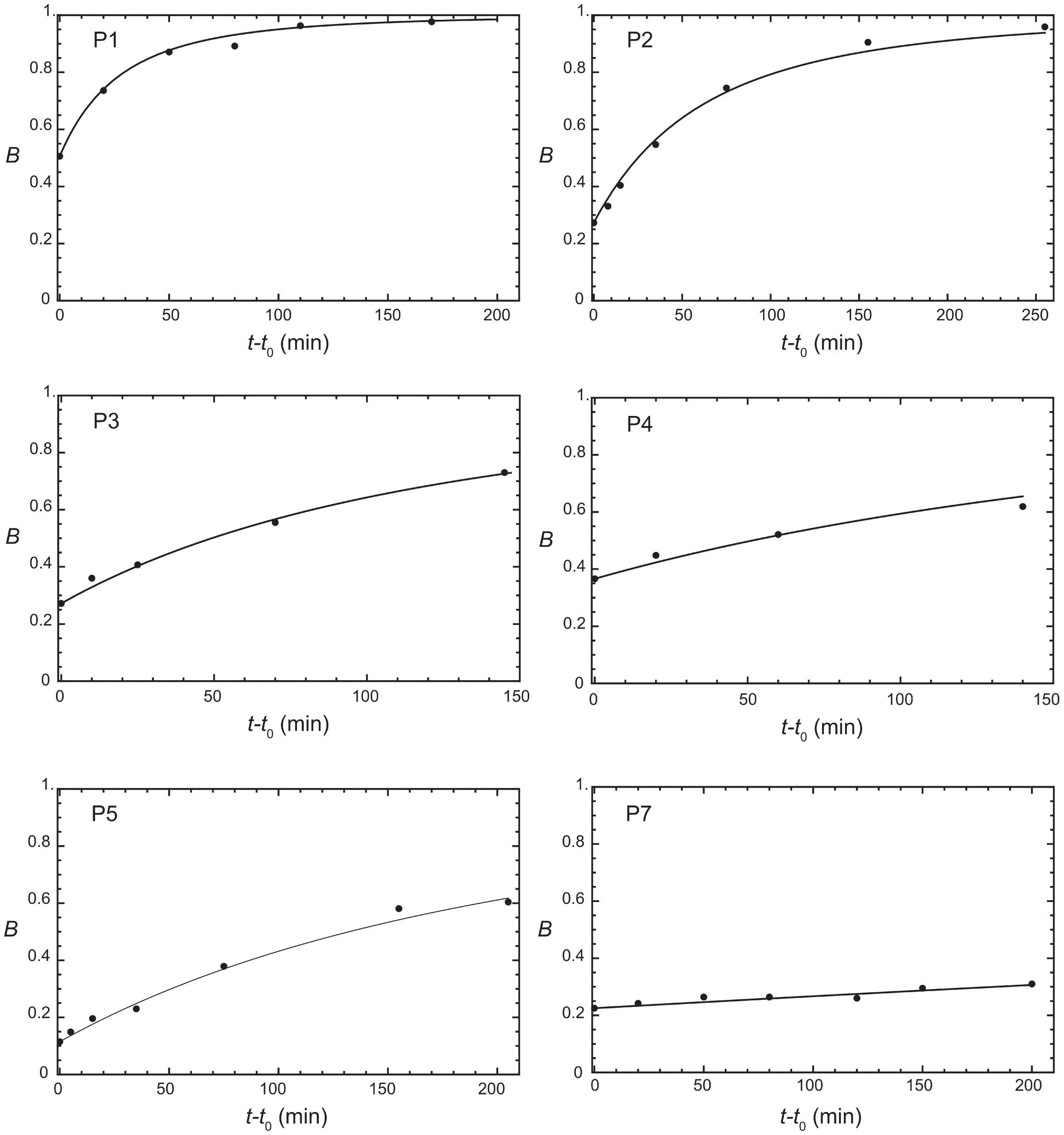


Figure 6. Evolution of the degree of randomness B during the randomization of Pn-PCL copolyesters (n = 1−5, 7) in the presence of $Ti(OBu)_4$ catalyst at 240 °C. Experimental data points and theoretical curves calculated from eq 3 and 10 with $k_1 = 0.02$ kg mol^{-1} min^{-1} and $k_2 = 7.8$ kg^2 mol^{-2} min^{-1}.

> mol ratio of the corresponding monomer units in copolymer. Indeed, it was shown in ref 50 that the relaxation of end groups requires only a few interchanges per chain, whereas complete copolymer randomization is achieved only when each ester bond has reacted in average once.

Consequently:

$$\frac{[\mathrm{EOH}]}{[\mathrm{LOH}]} = \frac{[\mathrm{EOTi}]}{[\mathrm{LOTi}]} = \frac{2E}{L} = \frac{2T}{L} \qquad (5)$$

Moreover

$$[\mathrm{EOH}] + [\mathrm{LOH}] = [\mathrm{OH}] \qquad (6)$$

$$[\mathrm{EOTi}] + [\mathrm{LOTi}] = [\mathrm{cata}]_0 \qquad (7)$$

and the theoretical limit of [ET] for a fully randomized copolyester is given by

$$[\mathrm{ET}]_\infty = \frac{2T}{2T+L}[\mathrm{ET}]_0 \qquad (8)$$

Introducing the mol fractions f_{ET} and f_{LT} of ET and LT dyads, with $f_{ET} + f_{LT} = 1$, eq 4 can be written

$$\frac{\mathrm{d}f_{ET}}{\mathrm{d}t} = (k_1 + k_2[\mathrm{OH}])[\mathrm{cata}]_0(f_{ET\infty} - f_{ET}) \qquad (9)$$

Therefore, from eq 2 and 9, the variations of B with time are given by eq 10.

$$\frac{\mathrm{d}B}{\mathrm{d}t} = (k_1 + k_2[\mathrm{OH}])[\mathrm{cata}]_0(1 - B) \qquad (10)$$

Since [OH] variations are described by eq 3, the model consists of two differential equations, eq 3 and 10, which can

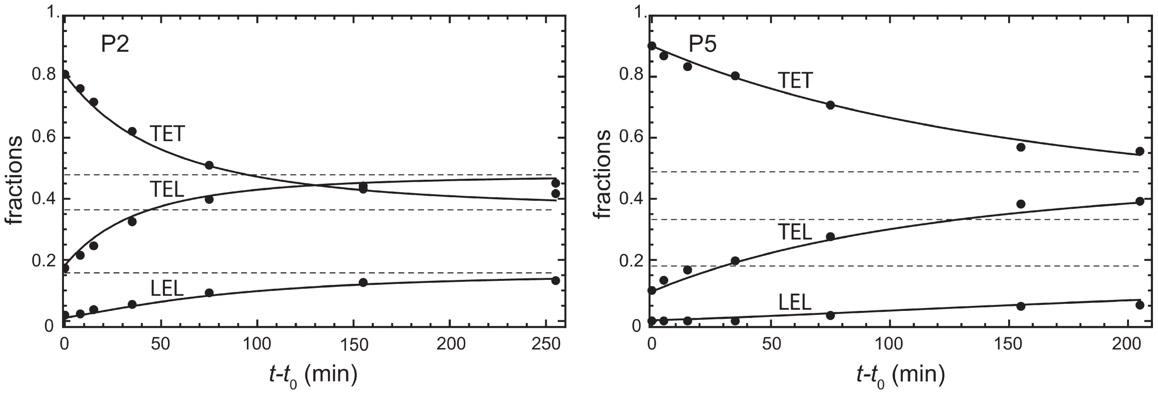


Figure 7. Evolution of the molar fractions of TET, TEL and LEL triads during the randomization of P2-PCL and P5-PCL copolyesters in the presence of $Ti(OBu)_4$ catalyst at 240 °C. Experimental data points and theoretical curves calculated from eq 1, 3 and 10 with $k_1 = 0.02$ kg mol^{-1} min^{-1} and $k_2 = 7.8$ kg^2 mol^{-2} min^{-1}. Dashed lines: Theoretical values of TEL (upper line), TET (middle line), and LEL (lower line) molar fractions for a completely random copolyester ($B = 1$).

easily be solved by standard integration and nonlinear optimization routines with initial time $t = t_0$ corresponding to the first sample with a free CL amount < 0.5%). Estimates of k_1 and of the corresponding standard errors were obtained from the reaction of methylester-terminated P7, in which only ester–ester interchanges can take place. Estimates of k_2 and of the corresponding standard errors were then determined from P1–P5 data fits. The results reported in Table 3 show that good fits were obtained (adjusted coefficient of determination $R^2 > 0.996$) and that k_2 values lie in the same relatively narrow range for all investigated polyester–CL systems.

This is also illustrated in Figure 5, which presents the linear fit of initial reaction rate r_0 against initial hydroxy group concentration. Slope value leads to $k_2 = 7.8 \pm 0.8$ kg^2 mol^{-2} min^{-1} and intercept to $k_1 = 0.02 \pm 0.01$ kg mol^{-1} min^{-1}, thus clearly showing the predominance of hydroxy–ester interchanges over ester–ester interchanges. It can be deduced from these values that ester–ester interchanges are predominant only when $[OH] < k_1/k_2 =$ ca. 2.6 mmol/kg, which corresponds to hydroxy-terminated PET of $\overline{M_n} > 770000$, far above what can be obtained by polyesterification processes.

Figure 6 presents the theoretical variations of B calculated with these rate constant values for the randomization of P1–P5 and P7 with CL and the corresponding experimental data, showing a very good agreement. The same is found for the comparison of theoretical and experimental variations of TET, TEL, and LEL triad mol ratios, as illustrated in Figure 7. From these figures, it is clear that higher OH concentrations (i.e., lower molar masses) lead to faster randomization kinetics. For instance, P1-PCL randomization is complete within 90 min while high-molar-mass P4-PCL or P5-PCL are not random even after more than 210 min. For these high-molar-mass copolyesters, Figure 5 shows that initial OH–ester randomization rate is ca. 10 times higher than that the rate corresponding to ester–ester interchanges. The randomization of high-molar-mass copolyesters in the presence of $Ti(OBu)_4$ catalyst is governed by OH–ester interchanges and reaction rate is proportional to OH end group content.

Conclusion

Copolyester randomization kinetics was studied on PET–PCL copolyesters. Since PCL was formed in situ by polymerization of CL monomer in molten PET, no homogenization step was required and randomization kinetics could be followed as soon as CL polymerization was complete, a few minutes after catalyst introduction. A randomization mechanism involving Ti-catalyzed parallel second-order ester–ester interchanges and hydroxy–ester interchanges is proposed and perfectly fits with the experimental values of the degree of randomness obtained on a series of PET of various molar masses and end group content. The parallel decrease of OH concentration due to polycondensation between hydroxyethyl end groups was taken into account in the overall mechanism. Some reasonable assumptions were made: (i) The contributions of carboxy–ester interchanges and of noncatalyzed reactions are negligible, (ii) direct and reverse interchange reactions present similar rate constants, and (iii) rapid interchanges take place between hydroxyalkyl and alkoxytitanium groups, leading to constant LOH/EOH and LOTi/EOTi ratios. Hydroxy–ester interchange reactions were found to be the predominant reactions involved in copolyester randomization, even for high molar-mass copolyesters. As a consequence, the nature and concentration of hydroxyl end groups present in industrial copolyesters play a major role in their randomization and should be carefully controlled for reliable randomization kinetics studies and reliable synthesis of copolyesters by homopolyester melt blending.

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