Mechanism of Exchange in PBT/PC and PET/PC Blends. Composition of the Copolymer Formed in the Melt Mixing Process

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ABSTRACT: Mechanisms operating in the exchange reactions occurring in the melt mixing processes of Bisphenol A polycarbonate (PC) with poly(butylene terephthalate) (PBT) and poly(ethylene terephthalate) (PET) blends have been investigated making use of appropriate polymer samples, capped or containing reactive chain end groups. The exchange process may proceed by two different mechanisms: a direct exchange reaction between inner functional groups located inside the polymer chains, i.e., inner−inner, or by attack of reactive chain ends functional groups (outer) on inner groups, i.e., outer−inner. It is shown that the distinction between the two processes can be conveniently made by determining the composition of the copolymer formed in the exchange reaction. The inner−inner mechanism occurs only in the reaction between end-capped or high molar mass PBT/PC or PET/PC samples, and it was found that the molar composition of the copolymer formed is always equal to the feed ratio of the two homopolymers and independent from the reaction time. The outer−inner mechanism occurs in the presence of hydroxyl or carboxyl reactive chain ends in PBT and PET samples. The reaction proceeds by the attack of the reactive end groups on the PC chains, originating block copolymers of PC and PBT and low molar mass PC with phenol end groups which are unreactive. The reaction stops right after the reactive end groups are consumed. The amount and the composition of the copolymers generated in the reactions are found to be constant as a function of time. The copolymer composition shows an excess of PBT or PET units with respect to the feed molar ratio. These results indicate that monitoring the composition of the copolymer formed in each case is diagnostic for establishing the mechanism of the reaction. The approach used here allows control of the composition and yield of the copolymer to be produced, and it is applicable to other systems where exchange reactions occur.

Introduction

In recent years considerable interest has arisen in the study of the exchange reactions which may occur during the melt mixing processes of polymers containing reactive functional groups (ester, carbonate, amide, etc.).[1−26]

End-group-activated exchange, or catalyst-activated exchange, may occur in such systems below 300 °C,[1−26] whereas both thermal activated exchange (i.e., without catalysts) and thermal decomposition occur above 300 °C.[5,11,20,26]

In the following, we wish to discuss the exchange processes which may occur in these systems (Figure 1), paying attention to the experimental parameters that can be used to discriminate among the various mechanisms.

A general question, when dealing with exchange reactions, is the detailed mechanism by which they take place: by direct exchange between inner functional groups (i.e., located inside the polymer chains) as shown in reactions A and B of Figure 1, or by attack of outer functional groups (i.e., reactive chain ends) on inner groups (reactions C and D of Figure 1).

Our analysis is based on the distinction between inner groups exchange (called here inner−inner) and active chain ends exchange (called here outer−inner).

The inner−inner intramolecular exchange process (Figure 1, reaction A), produces a low molar mass cyclic homopolymer and a shorter linear homopolymer chain. When an intermolecular inner−inner exchange process occurs between two homopolymers of different structure (Figure 1, reaction B), two linear copolymer chains are formed. The copolymer chains thus generated can, in turn, undergo exchange according reactions A or B. When a sufficient number of exchanges have occurred, both linear and cyclic random copolymer chains would be present in the mixture.[22,23]

When the exchange occurs by an intramolecular outer−inner process (reaction C), a cyclic homopolymer and a shorter linear homopolymer chain are produced, similar to reaction A.

The intermolecular outer−inner reaction (Figure 1d) does not produce two copolymer chains (as in Figure 1b), because only the polymer chain bearing active chain ends (outer groups) can attack the inner group of the other polymer, yielding a copolymer molecule plus a shorter linear homopolymer chain.

In this case, the homopolymer reacting through its inner groups undergoes a random scission process, and its molar mass should vary according to the random scission law.[20]

To distinguish between inner−inner and outer−inner processes, one may look at several parameters such as (i) composition of the copolymer formed in the exchange reaction, (ii) dependence of the reaction extent on the concentration of active chain ends, and (iii) dependence of the reaction rate from the molecular weight of the homopolymer reacting through its active chain ends.

In the ester exchange reaction, a popular example among these systems, the formation of copolymer molecules has been ascertained to occur as the result of two concurrent processes: the initial formation of a block copolymer from homopolymers and the process in which

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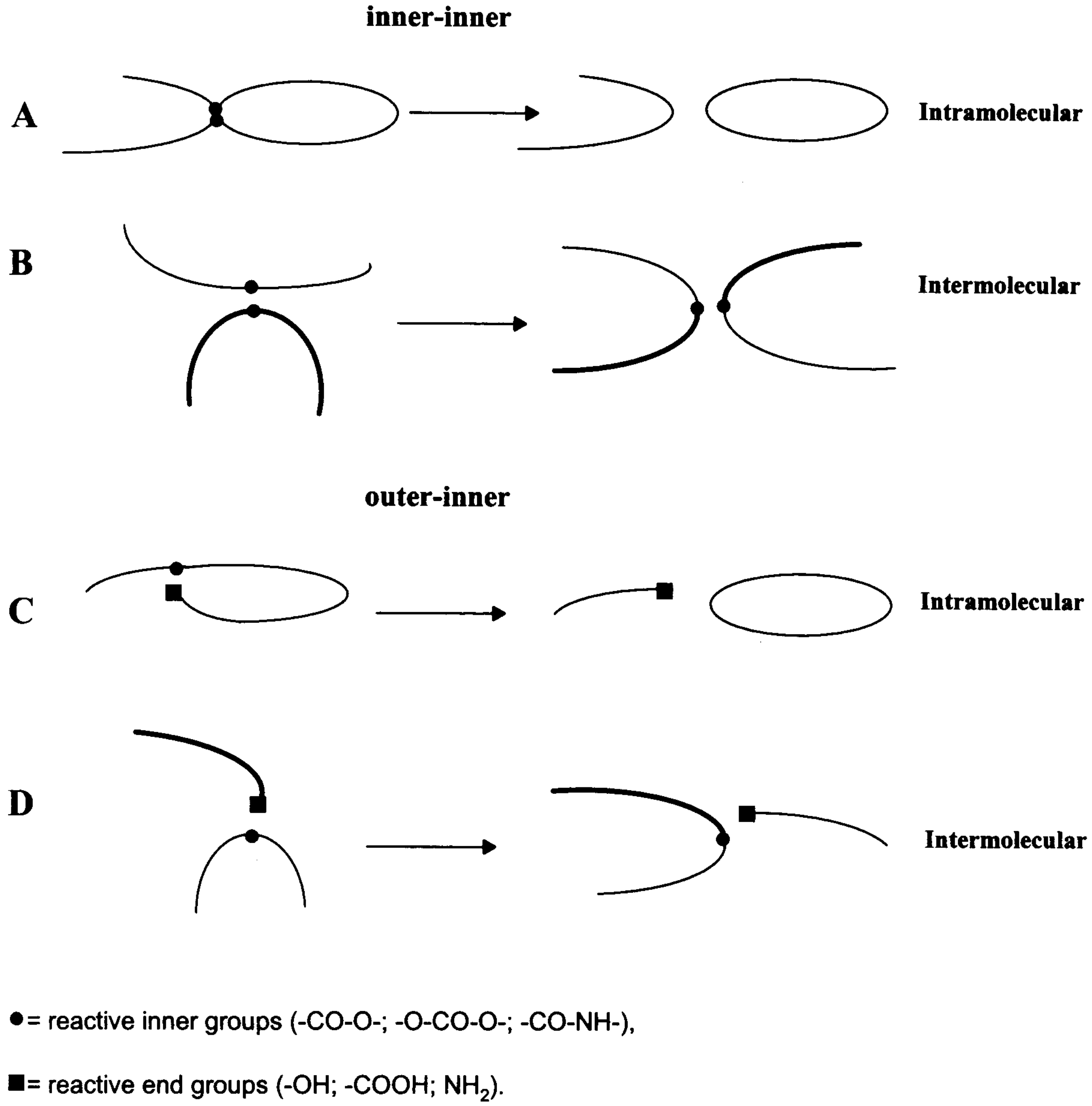


Figure 1. Schematic representation of the exchange reaction mechanisms which can occur in polymers containing reactive functional groups: (a) the exchange involves the inner groups of the same chain; (b) the exchange involves the inner groups of two chains; (c) the exchange involves the outer and inner reactive groups of the same chain; (d) the exchange involves the outer and inner reactive groups of different chains.

the copolymer rearranges itself in another copolymer with a random distribution of units along the copolymer chain.[22,23]

To distinguish the specific exchange mechanism involved in the reaction between two different homopolyesters, A and B, i.e., inner–inner or outer–inner, four cases can be hypothesized, which are sumarized in Table 1.

Assuming (case 1, Table 1) that, in an equimolar mixture of homopolyesters A and B, the exchange reaction takes place by direct interaction of two inner ester groups (assuming also that the reactivity of the two ester groups is nearly the same), the concentration of functional groups of species A and B is equal, and each species has the same probability of reacting.

Then, the composition of the AB copolyester formed is predicted to be close to 1:1 (feed ratio), independent of the extent of reaction, and the reaction shall proceed up to the complete transformation of the two homopolymers (Table 1).

Now assume that the exchange reaction takes place by active chain-ends (for instance, alcoholic groups in polyesters). If both homopolymers possess these reactive end groups (case 2, Table 1), in an equimolar mixture of them, the same result as above is predicted and the molar ratio of components in the copolymer formed should be 1:1.

Therefore, the latter experiment yields the same result as case 1, and it is not diagnostic to establish the mechanism of exchange.

However (case 3, Table 1), if only one of the homopolymers (A) possesses alcoholic reactive chain ends, only the latter shall be able to attack the inner ester groups of polyester B, thus cutting (statistically) the polyester B chains in two pieces.

Provided that the homopolymer A has a relatively high molecular weight, the AB copolymer initially formed shall contain an excess of A units.

Considering that each exchange reaction generates an alcoholic end group of B type (not existing initially),

Table 1. Copolymer Composition Expected for the Different Mechanisms of Exchange Reactions Occurring in the Melt Mixing of Two Homopolymers A and B

inner/inner^{a,b} catalyst is needed below 300 °C	**outer inner**^{a} catalyst is not needed		
case 1	case 2	case 3	case 4
	homopolymers A and B possess reactive chain ends	only homopolymer A possess reactive chain ends	only homopolymer A possess reactive chain ends
	reactive end groups are regenerated	reactive chain ends of type B are generated and participate to the reaction	unreactive chain ends of type B are generated and do not participate to the reaction
copolymer AB 50/50 (mole) is formed	copolymer AB 50/50 (mole) is formed	copolymer AB formed in early stages contains an excess of A chains	copolymer AB contains an excess of A units
		copolymer AB formed in later stages has composition 50/50 mole	
copolymer composition is independent of extent of reaction	copolymer composition is independent of extent of reaction	copolymer composition is dependent of extent of reaction	copolymer composition is independent of extent
reaction goes to completion	reaction goes to completion	reaction goes to completion	the exchange reaction stops as soon as reactive chain ends are consumed

[a] Initial feed: equimolar mixtures of homopolymers A and B. [b] Equal reactivity of inner groups in homopolymers A and B is assumed.

which shall then participate to the reaction, A and B end groups shall both be present in the reaction mixture.

Therefore, the composition of the copolymer formed in the later stages of the reaction is expected to equilibrate and to come close to 1:1 ratio (i.e., with the progress of the exchange reaction, this system behaves as in case 2, where both types of end groups are present). This experiment (case 3) is diagnostic, allowing a discrimination between the two mechanisms of copolyester formation.

In a final example (case 4, Table 1), only one of the homopolymers possesses alcoholic reactive chain ends (type A), and only these shall be able to attack the inner ester groups of polymer B.

However, unlike case 3, the chain ends of type B generated in the exchange are assumed to be unreactive, and the reaction shall stop when the reactive chain ends initially present shall be consumed.

In this case the AB copolymer formed shall contain an excess of A units, independent of the extent of exchange.

In a previous work[22] we have performed an experiment where a high molar mass poly(ethylene terephthalate) (PET) sample was completely freed from the low molar mass oligomers.

The latter was then reacted with an equimolar amount of a poly(ethylene adipate) (PEA) sample terminated with reactive hydroxyl end groups, and the exchange kinetics at 280 °C was followed by analyzing the reaction mixture by ^{1}H NMR and by fast atom bombardment mass spectrometry (FAB-MS).[22]

We observed that the copolyester initially formed in the exchange reaction is a block copolymer containing an excess of EA units, as should be expected if the reaction would proceed by the attack of PEA hydroxyl end groups on the inert PET chains (Figure 1D).

PET hydroxyl end groups (initially absent) generated in the course of the exchange reaction were also able to react with PEA chains, and in the later stages of the reaction the copolyester microstructure approached a random distribution and an equimolar composition,[22,23] in agreement with the above discussion.

The approach outlined, based on the determination of the copolymer composition as a function of the extent of exchange, appears applicable as a general mechanistic criterion for exchange reactions and for the prediction of the copolymer composition attainable in specific systems.

Ester exchange reactions are also involved in the melt mixing processes of poly(butylene terephthalate)/Bisphenol A polycarbonate (PBT/PC)[3−9] and poly(ethylene terephthalate)/Bisphenol A polycarbonate (PET/PC) blends [3,10−14] that have been extensively investigated.

We found it therefore interesting to investigate the dependence of copolymer composition on the extent of reaction in these systems and to compare it with that observed previously in the case of ester−ester exchange.

Experimental Section

Materials. Chemicals were analytical-grade commercial products, supplied by Aldrich and Merck, appropriately purified before use. Poly(Bisphenol A carbonate) ($\eta_{inh} = 0.48$ in $CHCl_3$ at 30 ± 0.1 °C), poly(1,4-butylene terephthalate), and poly(ethylene terephthalate) ($\eta_{inh}= 0.81$ and 0.5, respectively, in phenol/tetrachloroethane (60/40 v/v) at 30 ± 0.1 °C) were purchased from the Aldrich Chemical Co (Italy) and dried at 60 °C for a week, under vacuum, before use.

Deuderated solvents were purchased from Merck.

Synthesis of Polyesters. (a) PBT with Hydroxyl Terminal Groups. PBT samples with alcoholic end groups were prepared by solution polymerization starting from terephthaloyl dichloride and an appropriate excess of the butanediol. The synthesis of PBT with hydroxyl end groups and a molar mass of 3000 is reported below.

A 0.12 mol (7.44 g) portion of butanediol and 50 mL of a mixture of (70/30 v/v) 1,1,2,2-tetrachloroethane/tetrahydrofuran (TCE/THF) were placed in a three-necked flask. A 0.10 mol (20.20 g) portion of terephthaloyl dichloride solubilized in 50 mL of TCE/THF, and 0.2 mol of *N*,*N*-dimethylanyline in 50 mL of TCE/THF were simultaneously added dropwise to the butanediol solution, under stirring. The reaction mixture was maintained at 90 °C, and after 24 h 0.2 mol of butanediol was added, to eliminate the acid chloride residue. The solution was maintained at 90 °C for 1 h. After that the solvent was removed by vacuum distillation and the solid residue was washed several times with boiling acetone to eliminate unreacted monomers and the amine chlorohydrate. The low molar mass oligomers were extracted with THF at room temperature for 12 h. The solid residue was filtered and dried at 60 °C under vacuum for 3 days. A white powder was obtained, yield 70%. The sample was characterized by ^{1}H NMR analysis in deuderated TCE at 70 °C. The amount of hydroxyl end groups obtained by ^{1}H NMR was 0.7 mol/kg and a $M_n = 3000$ and $X_n = 14$ were calculated.

The other two samples with a M_n 6000 and 18 000 were prepared using a butanediol/terephthaloyl dichloride ratio of

1:1.1 and 1:1.05, respectively. In these cases the low molar mass oligomers were extracted with a 70/30 v/v THF/TCE mixture. The amounts of hydroxyl end groups were found 0.34 and 0.12 mol/Kg, respectively.

(b) PBT with Capped Chains. The end capping of poly(butylene terephthalate) has been performed by reacting benzoyl chloride (BZCl) with hydroxyl-terminated PBT (MM 3000) in TCE, at 100 °C, using pyridine as acid acceptor. In a typical procedure: 0.1 mol of BZCl in 50 mL of TCE and 0.2 mol of pyridine in 50 mL of TCE were slowly added dropwise to 5 g of PBT dissolved in 150 mL of TCE. The reaction mixture was maintained at 100 °C for 24 h. The solvent was removed by vacuum distillation, and the solid residue was washed several times with boiling acetone and dried at 70 °C under vacuum, for 2 days.

The sample was characterized by ^{1}H NMR analysis in deuterated TCE at 70 °C.

(c) PET with Carboxylic Acid Terminal Groups. The synthesis of PET with carboxylic acid end groups was performed by polymerization of the ethylene glycol with an excess (1.2) of terephthaloyl dichloride and subsequent hydrolysis of the acid chloride end groups as described below.

A 0.1 mol portion of ethylene glycol and 50 mL of dried fresh distilled DMF were placed in a three-necked flask; 0.12 mol of terephthaloyl chloride dissolved in 70 mL of DMF and 0.2 mol of pyridine in 50 mL of DMF were simultaneously added dropwise to the glycol, under vigorous stirring. The reaction mixture was maintained at 90 °C, under nitrogen flow, and after 24 h a small amount (0.2 mol) of terephthaloyl dichloride was added. The solution was maintained at 70 °C for 1 h. After that, 2 mL of water and 0.1 mol of pyridine were added, to hydrolyze the acid chloride end groups. After 5 h the solvent was removed by vacuum distillation (2 Torr) and the solid residue was washed twice with boiling ethanol and several times with boiling acetone. The low molar mass oligomers were extracted with THF at room temperature for 12 h. The white powder was dried at 60 °C under vacuum, for 3 days, yield 80%.

The sample was characterized by ^{1}H and ^{13}C NMR in $CDCl_3$/TFA (70/30 v/v) at room temperature. No appreciable amounts of signals of the type AA′BB′, centered at 3.9 and 4.5 ppm, typical of diethyleneglycol units were observed in the ^{1}H NMR spectrum. These units might be generated by side reactions occurring during the synthesis.

The amount of carboxylic acid end-groups was obtained by titration with a 1×10^{-3} M KOH/methanol solution using DMF as solvent, at 60 °C, as described in the literature.[14] Carboxylic acid end groups (0.8 mol/Kg) were found corresponding to a M_n of 2500.

Reactive Blending. The reaction of high molar mass PET/PC and PBT/PC blends was carried out in a Brabender mixer at 45 rpm, under nitrogen flow, in the presence of $Ti(OBut)_4$ as trans-esterification catalyst. Typically, 40 g of equimolar (in repeat units) of PBT/PC blend (53/47 w/w) were melt-mixed at 240 °C, whereas a 50/50 w/w (43/57 mol/mol) PET/PC blend were melt mixed at 270 °C. The catalyst (0.1%, w/w) was added after two min of mixing and this was considered as time zero. About 2 g of blend were sampled from the Brabender cup at 2, 4, 6, 8, 10, 20, 30, 40, 60, 75, 90 and 120 min.

The reactions of high molecular weight PC with hydroxyl-terminated PBT, benzoate-capped PBT, and carboxyl-terminated PET blends were carried out in a glass reactor equipped with a mechanical stirrer, under nitrogen flow.

All samples obtained in the reactive mixing experiments were subjected to selective extraction (see below) and were characterized by NMR spectroscopy.

Selective Extraction. The blend samples obtained in the melt-mixing experiments were selectively extracted with THF and TCE in sequence.

One gram of blend sample was refluxed with 50 mL of THF for 6 h, then filtered, and washed several times with fresh THF, and the residue (A) was dried at 50 °C overnight, under vacuum. The THF solution was vacuum distilled and the solid material recovered was constituted of unreacted PC. Fraction A (i.e., the portion insoluble in THF), was treated with 50 mL of TCE at 40 °C for 6 h, then filtered, and washed several times with fresh TCE. The portion insoluble in TCE was dried at 70 °C overnight, under vacuum, and it proved to be constituted of unreacted PBT or PET. The TCE solution was vacuum distilled and the solid material recovered was found constituted of PBT/PC or PET/PC copolymers.

The fraction soluble in TCE was not present near the end of the reaction, since the PBT/PC or PET/PC copolymers became soluble in THF, after which the exchange reaction went to completion (10 min for PBT/PC blend and 4 min for PET/PC blend).

All fractions obtained by selective extraction were characterized by NMR spectroscopy.

NMR Analysis. ^{1}H and ^{13}C NMR spectra were obtained on a Bruker A-CF-200 spectrometer using $CDCl_3$, deuterated 1,1,2,2-tetrachloroethane (TCE-d_2), deuterated trifluoroacetic acid (TFA), and tetramethylsilane (TMS) as internal standard. The ^{13}C NMR spectra were recorded with the following acquisition parameters: sweep width, 9800 Hz; 65 536 data points, giving a digital resolution of 0.299 Hz per point and an acquisition time of 3.4 s. A pulse width of 4 ms and a delay of 2 s were used for about 20 000 accumulations.

The ^{1}H and ^{13}C NMR chemical shift of main chain protons and carbon resonances of PC, PBT, and copolymers generated in the exchange reactions have been found in agreement with the literature[4] and are not reported here.

PBT with hydroxyl and benzoate end groups were characterized by ^{1}H NMR, whereas the PET with carboxyl end groups was characterized by ^{13}C NMR.

The ^{1}H NMR spectrum of hydroxyl-terminated PBT, recorded at 70 °C in TCE-d_2, shows signals at 8.09 ppm due to aromatic protons, at 4.41 and 1.95 ppm assigned to methylenes α and β,γ to the ester groups, respectively. A triplet centered at 3.70 ppm assigned to the methylene adjacent to hydroxyl end groups and a multiplet between 1.7 and 1.9 ppm due to methylene in β and γ, are also present.

In the ^{1}H NMR spectrum of the benzoate-capped PBT sample, besides the main chain protons (at 1.95, 4.41, and 8.09 ppm), new aromatic proton signals at 7.31−8.08 ppm due to benzoate ester end groups are present.

The ^{13}C NMR spectrum of PET with carboxyl end groups was recorded in $CDCl_3$/TFA (70/30, v/v) at room temperature; it showed signals due to the main chain PET carbon resonances (at 62.96, 129.62, 133.7, and 165.33 ppm), the signal at 171.8 ppm due to carbonyls of terephthalic acid end groups, the signals at 132.62 and 134 ppm corresponding to the quaternary aromatic carbons of terephthalate units. We duplicated the ^{13}C NMR spectrum of this sample in DMSO-d_6 at 90 °C, and it was found identical to the previous one, therefore excluding the occurrence of degradation reaction induced by the presence of TFA.

The carbon resonances corresponding to the copolymer sequences generated in the catalyzed exchange reaction of PC and PET (Scheme 2) have been identified and assigned as follows: **1**, 120.3; **2**, 62,96; **3**, 121; **4**, 62.96; **5**, 66; **6**, 63.9; **7**, 65.8; **8**, 114 ppm. The proton resonances have been assigned according to the literature.[10−14]

Material Balance Calculation. The material balance of the catalyzed reaction at 270 °C of PET/PC blends has been calculated by using the molar ratio of ethylene to terephthalate protons (Et/T, Table 2) and the intensities of the ^{13}C NMR signals corresponding to carbons identified in Scheme 1 and assigned above. The following equations have been used:

$$M_{A'} = [I_{(C1)}/I_{(C1,3,8)}]\cdot 43$$

$$M_{B'} = [I_{(C4)} + I_{(C2)} - I_{(C5)}/I_{(C2,4,5,6,7)}]\cdot 57\cdot \mathrm{Et/T}$$

$$M_{C'} = [I_{(C3)}/I_{(C1,3,8)}]\cdot 43$$

Table 2. Material Balance and Composition of the Copolymer Formed in the Melt Mixing of Catalyzed PC/PBT Blend and Uncatalyzed Blends of PC with Hydroxyl-Terminated and Benzoate-Capped PBT

catalyzed PC/PBT (240 °C)						uncatalyzed capped PBT/PC (290 °C)					uncatalyzed PC/PBT-OH (240 °C)						
reaction time (min)	wt % of extracted fractions[a]			copolym comp[b]	degree of randomness[c]	reaction time (min)	wt % of extracted fractions[a]			copolym comp[b]	reaction time (min)	PC/PBT3000					
	Cop	PC	PBT				Cop	PC	PBT			WC[d]	CC[e]	WC[d]	CC[e]	WC[d]	CC[e]
0	0	54	46		0	5	38	35	27	50	5	54	72	54	74	60	78
2	25	40	35	52	0.02	10	65	19	16	51	10	53	73	53	75	61	77
5	53	24	23	50	0.1	30	100			51	30	53	71	53	74	59	79
8	94	3	2	47	0.2	60	100			50	60	52	73	52	75	59	78
10	100			50	0.26						120	55	73	55	74	60	79
15	100			50	0.29												
20	100			50	0.32												
30	100			50	0.43												
40	100			50	0.56												
50	100			50	0.69												
60	100			50	0.81												
75	100			50	0.91												
90	100			50	0.94												
120	100			50	0.96												

[a] See experimental part. [b] Molar ratio of terephthalate with respect to Bisphenol A units in the copolymer, as obtained by 1H NMR (standard deviation ±0.1%). [c] Calculated by ^{1}H NMR according to ref 4 (standard deviation ±0.01%). [d] Weight of copolymer (standard deviation ±1%). [e] Copolymer composition, i.e., molar ratio of terephthalate to Bisphenol A units (standard deviation ±1%).

Table 3. Material Balance and Molar Amount of Structural Units Present in the Copolymer Formed in the Catalyzed Reaction of PC/PET Blend at 270 °C

mixing time (min)	wt % of exctracted fractions[a]			copolym comp[b]	Et/T[c]	T/B[d]	TG % wt loss[e]	NMR % wt loss[f]		NMR molar amt of copolymer structural units[g]				
	Cop	PC	PET					ETC	CO_2	M_A	M_B	M_C	M_D	M_E
0		50	50		1	1.32				43	57			
2	70	13	17	57	1	1.32	0.3	N.M.	0.2	38.4	51.5	4.05	5.05	1.0
4	100			57	0.99	1.32	0.8	0.2	0.6	36.1	47.4	6.2	7.2	3.1
6	100			57	0.98	1.32	1.0	0.3	0.6	33.3	43.8	9.4	10.4	3.1
8	100			57	0.97	1.32	1.3	0.45	0.9	29.6	41.3	10.6	13.8	4.8
10	100			57	0.95	1.32	1.5	0.6	1	28.3	40.8	11.6	14.1	5.2
20	100			57	0.88	1.30	4	2.8	1.8	20.5	35	18	15.7	10.8
30	100			57	0.81	1.31	6.5	4.3	2.4	15.7	34	23.5	11.1	15.7
40	100			57	0.69	1.31	9.3	7	3.2	8.8	32.2	29.8	3.5	25.7
60	100			57	0.68	1.30	12	7.6	4.2	0	30	35		35
90	100			57	0.67	1.32	13	7.6	4.2	0	30	35		35
120	100			57	0.67	1.30	14	7.6	4.2	0	30	35		35

[a] See experimental part. [b] Molar ratio of terephthalate to Bisphenol A units, obtained by ^{1}H NMR (standard deviation ±0.05%). [c] Molar ratio of ethylene to terephthalate units of the unfractionated blends, obtained by ^{1}H NMR (standard deviation of ±0.01%). [d] Molar ratio of terephthalate to bisphenol A units of the unfractionated blends, obtained by ^{1}H NMR (standard deviation of ±0.02%). [e] Obtained by isothermal thermogravimetric analysis at 270 °C (standard deviation of ±0.1%). [f] % weight loss of ethylene carbonate (ETC) and CO_2, as calculated by ^{1}H NMR (standard deviation of ±0.1%), see experimental part. [g] Calculated by ^{13}C NMR (standard deviation of ±0.02%), see experimental part.

$$M_{D'} = [2I_{(C5)}/I_{(C2,4,5,6,7)}]\cdot 57\cdot \mathrm{Et/T}$$

$$M_{E'} = [2I_{(C6)}/I_{(C2,4,5,6,7)}]\cdot 57\cdot \mathrm{Et/T}$$

$$M_{(ETC)} = [57 - (57\cdot \mathrm{Et/T})]$$

$$M_{(CO_2)} = M_{E'}$$

ETC is ethylene carbonate; $M_{A'}$, $M_{B'}$, $M_{C'}$, $M_{D'}$, and $M_{E'}$ represent the molar amount of structural units of unfractionated PET/PC blend samples, relative to the feed. These data have been normalized to 100 to obtain the molar amount of copolymer structural units and are reported in Table 2. The values 43 and 57 are the molar amounts of PC and PET in the feed.

$M_{(ETC)}$ and $M_{(CO_2)}$ represent the molar amount, relative to the feed of ethylene carbonate and CO_2, lost from the reacting system. The weight losses of ETC and CO_2 have been calculated as follows:

$$W_{(ETC)} = M_{(ETC)}\cdot[88/(43\cdot 254 + 57\cdot 192)]$$

$$\mathrm{W}_{(CO_2)} = \mathrm{M}_{(CO_2)}\cdot[44/(43\cdot 254 + 57\cdot 192)]$$

The values 88 and 44 are the molar masses of ethylene carbonate and CO_2; 254 and 192 are the molar masses of the repeat units of PC and PET, respectively.

Thermogravimetry. A Perkin-Elmer thermal analyzer TGS-2 was used to determine the weight loss. Two milligrams of the 50/50 (w/w) PC/PET blend, containing 0.1% of $Ti(OBut)_4$ as catalyst, was maintained at 270 °C for 2 h, under nitrogen at a flow rate of 60 mL/min. Values are reported in Table 3.

Results and Discussion

PBT/PC Blends. To investigate the dependence of copolymer composition from the specific exchange mechanisms, some PBT samples bearing different types of end groups were synthesized and reacted in the melt, as a function of time, with a high molar mass PC sample.

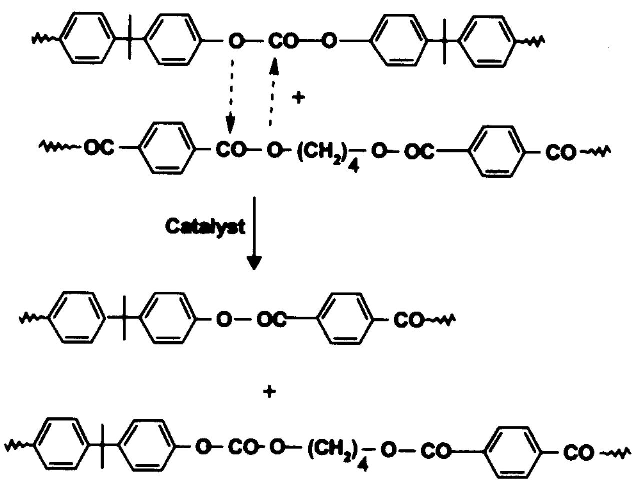
The reactions that can occur in this system are known[3−9] and are summarized in Scheme 1A−C.

The exchange reaction between high molar mass PBT and PC occurs already at 240 °C in the presence of a trans-esterification catalyst, likely by an inner−inner mechanism (Scheme 1a).

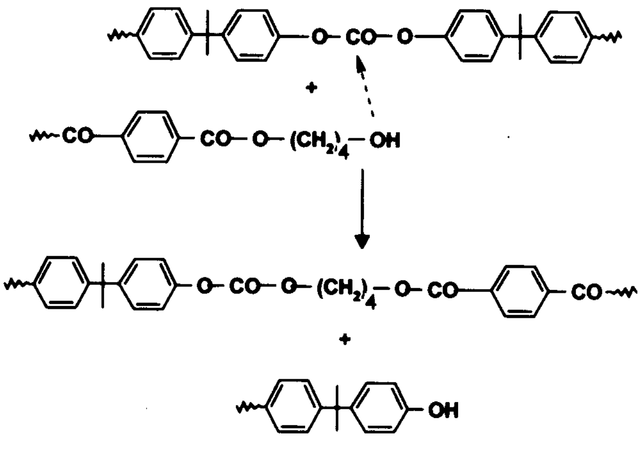
To explore the dependence of the copolymer composition from the inner−inner exchange mechanism, we

Scheme 1. Exchange Reactions Which Can Occur in the Melt Mixing of PBT/PC Blends

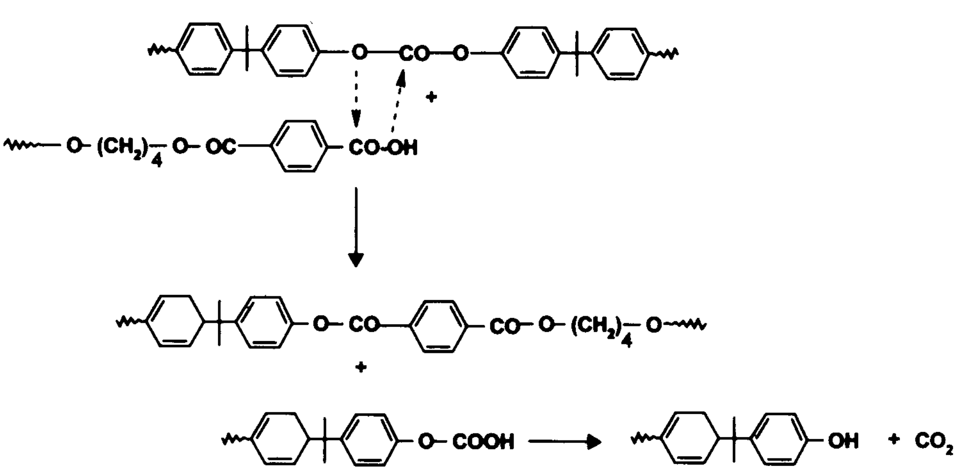
a. direct ester-carbonate exchange (inner-inner)



b. alcoholysis (outer-inner)



c. acidolysis (outer-inner)



have reacted an equimolar mixture of high molar mass PBT and PC at 240 °C in the presence of Ti(OBut)$_4$ as a function of time, in a Brabender mixer. PC/PBT blend samples taken at different time intervals were selectively extracted with THF and TCE in sequence (see Experimental Section) and characterized by NMR. THF

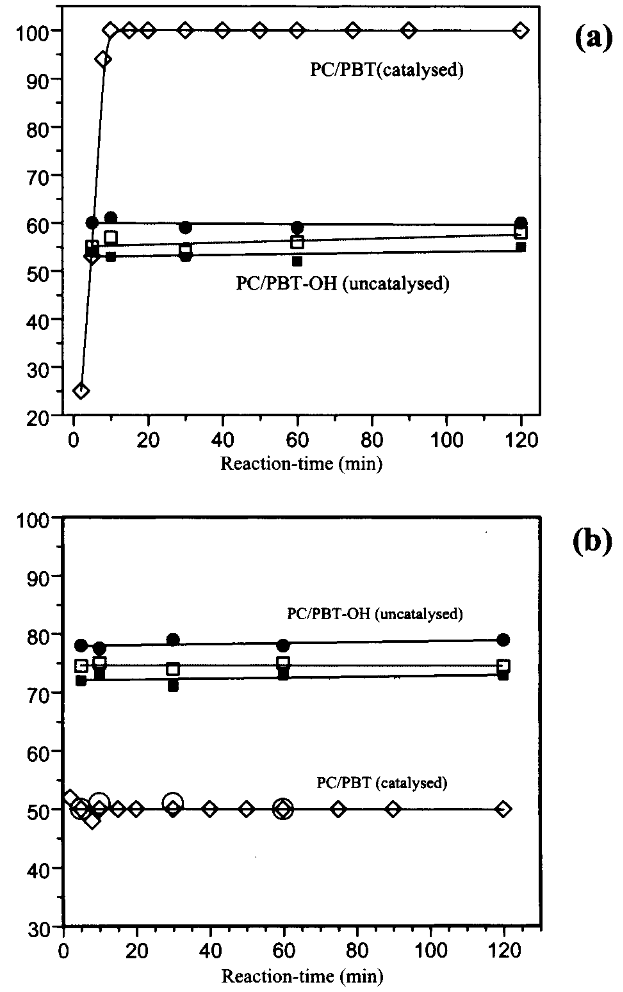


Figure 2. (a) Weight percent and (b) composition of the copolymer produced in the melt-mixing at 240 °C of (◇) catalyzed PC/PBT blend, (●) uncatalyzed PC/PBT18000 blend (□) uncatalyzed PC/PBT6000 blend, (■) uncatalyzed PC/PBT3000 blend, and (○) uncatalyzed capped PBT/PC blend (reacted at 290 °C).

is able to extract selectively the unreacted PC, whereas PC/PBT copolymers are soluble in TCE at room temperature. The residue of the extraction is constituted by unreacted PBT.

Initially, a block copolymer is formed, which becomes randomized as the reaction time increases. The degree of randomness of the copolymers formed (Table 2) has been monitored by ^{1}H NMR, according to the literature.[4]

The material balance of the reaction, reported in Table 2, shows that the weight of copolymer formed is 25% after 2 min and that the reaction goes to completion in about 10 min (Figure 2a).

The composition of the copolymer produced in the catalyzed reaction, indicated as molar ratio of terephthalate to Bisphenol A units (obtained by ^{1}H NMR), was monitored as a function of the reaction time and was found (Figure 2b) to be 50:50 (i.e., equal to the feed ratio of the two homopolymers), independent from the reaction time, as predicted (Table 1).

The uncatalyzed inner–inner exchange reaction between PC and a PBT sample with the chain ends capped by benzoate groups does not take place at 240 °C but it occurs only at higher temperature.[5,11,26]

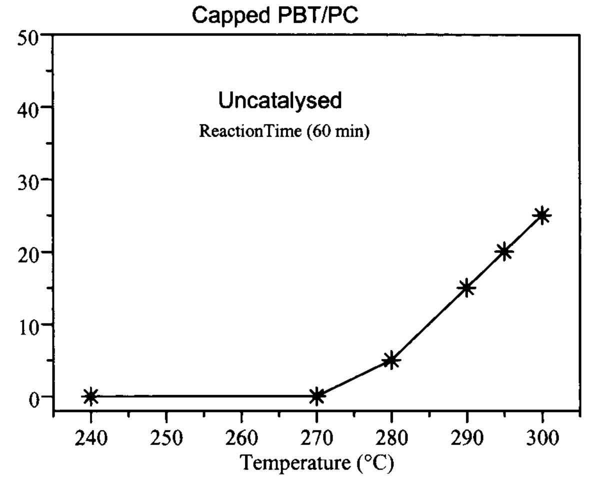


Figure 3. Extent of exchange (molar ratio of aromatic terephthalate triads at 8.21 ppm in the ^{1}H NMR spectra) of uncatalyzed capped PBT/PC blend samples melt-mixed for 60 min as a function of temperature.

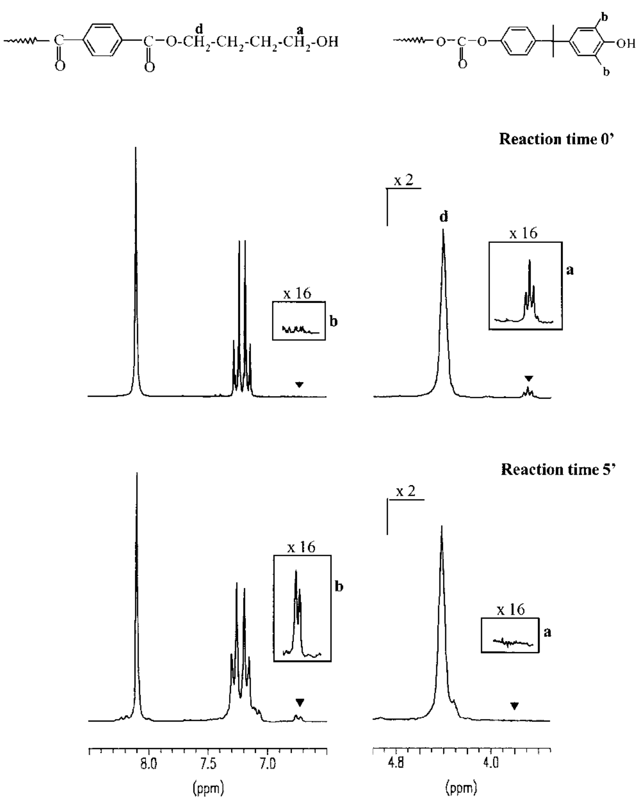
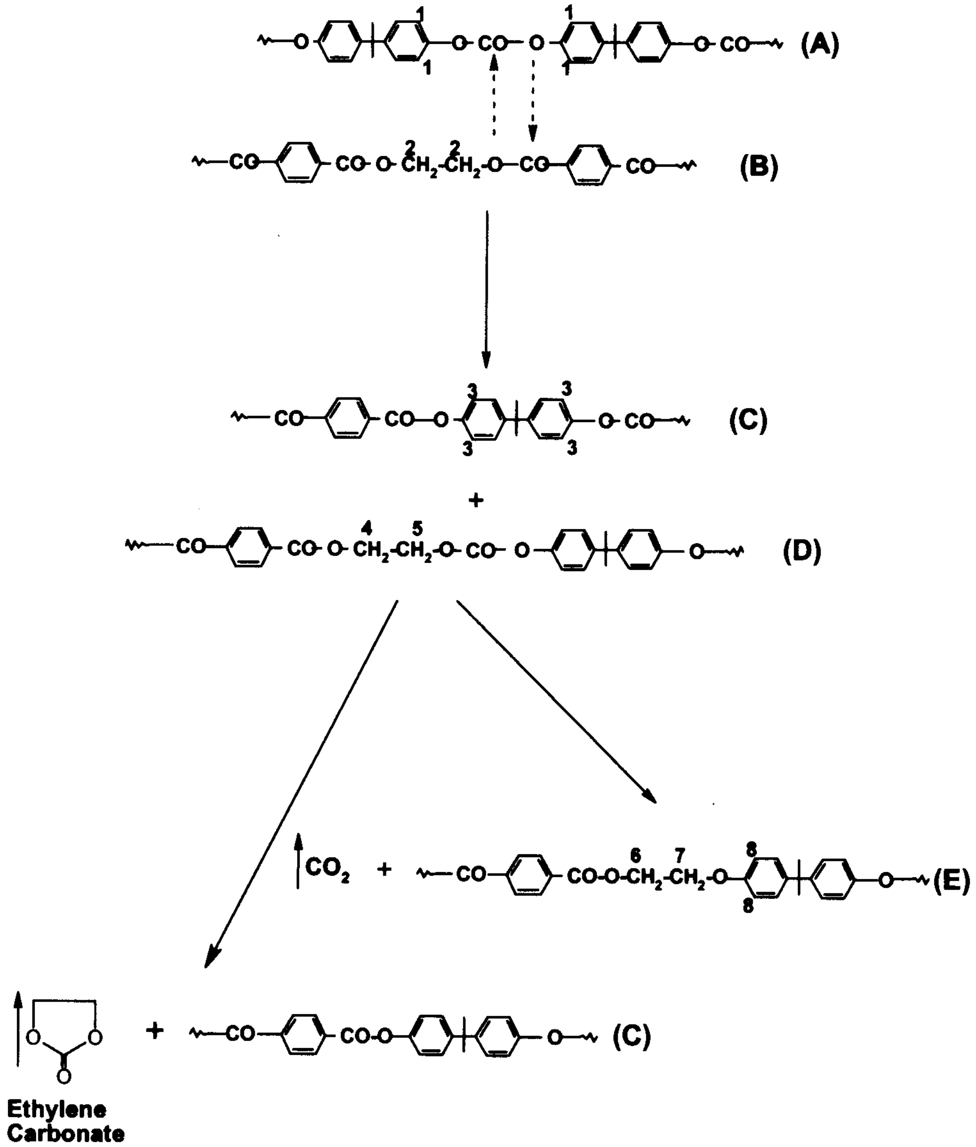


Figure 4. ^{1}H NMR spectra of uncatalyzed blend of hydroxyl terminated PBT (MM = 3000) with PC melt mixed at 240 °C for 0 and 5 min.

To ascertain the onset of the reaction, an equimolar blend was reacted for 60 min as a function of the temperature. The reaction was followed by monitoring the extent of exchange, i.e., the molar ratio of asymmetric aliphatic–aromatic terephthalate triad signal centered at 8.21 ppm in the ^{1}H NMR spectra. It was found that the reaction takes place at above 280 °C and that the extent of exchange increases with the temperature (Figure 3).

We have also detected, in comparable amounts to the above triad, the presence of the signal at 4.3 ppm due to the triad PC/butylenecarbonate/terephthalate formed in the ester–carbonate exchange (Scheme 1a). The latter triad should not be present if the exchange had occurred through carboxylic end groups formed by degradative processes of PBT chains.

Scheme 2. Exchange Reactions in the Catalyzed Melt Mixing of PET/PC Blend



Furthermore, benzoate-capped PBT heated at 290 °C for 1 h does not show formation of carboxyl and olefin end groups due to thermal degradation. The presence of olefin signals at 5–5.4 ppm was detected only in the ^{1}H NMR spectra of samples heated above 310 °C. The loss of cyclic butylenecarbonate through the thermal degradation of BPA–butylenecarbonate sequences[5] has been observed in valuable amounts at temperature above 300 °C.

In Table 2 are reported the weight and the composition of the copolymer produced when an equimolar blend of capped PBT/PC was reacted at 290 °C as a function of time. It can be observed that 35% of the copolymer weight is formed after 5 min and that the reaction goes to completion at above 10 min. The molar ratio of terephthalate to Bisphenol A units of the extracted copolymer was found to be 50:50 (Figure 2b), i.e., equal to the feed ratio of the two homopolymers, therefore indicating the occurrence of an inner–inner exchange mechanism. This result is in agreement with the predictions and also with the results obtained with the catalyzed reaction.

The exchange reaction of high molar mass PC with a PBT sample containing hydroxyl end groups is likely to occur by an outer–inner mechanism (Figure 1D, Scheme 1b), and it does not need the presence of catalysts. The reaction proceeds by the attack of the hydroxyl end groups on the PC chains, giving origin to block copolymers of PC and PBT joined with butylcarbonate units and to low molecular weight PC with phenol end groups. The latter are unreactive at this temperature (240 °C), and therefore the reaction stops right after the reactive hydroxyl end groups of PBT are consumed.

To investigate the dependence of active chain end concentration on the copolymer composition, three samples of PBT bearing OH end groups with increasing molar mass (3000, 6000, 18 000) were reacted with PC at 240 °C as a function of reaction time.

The reactions were monitored by ^{1}H NMR, following the intensity changes of some pertinent peaks as shown in Figure 4 in which a blend of high molar mass PC and PBT (MM = 3000) with OH end groups reacted for 0 and 5 min is reported, as an example. It can be observed that already after 5 min of reaction the signal at 3.70 ppm assigned to the methylene (**a**) adjacent to OH group, disappears and a signal at 6.75 ppm due to aromatic protons (**b**) of phenol groups appears (Figure

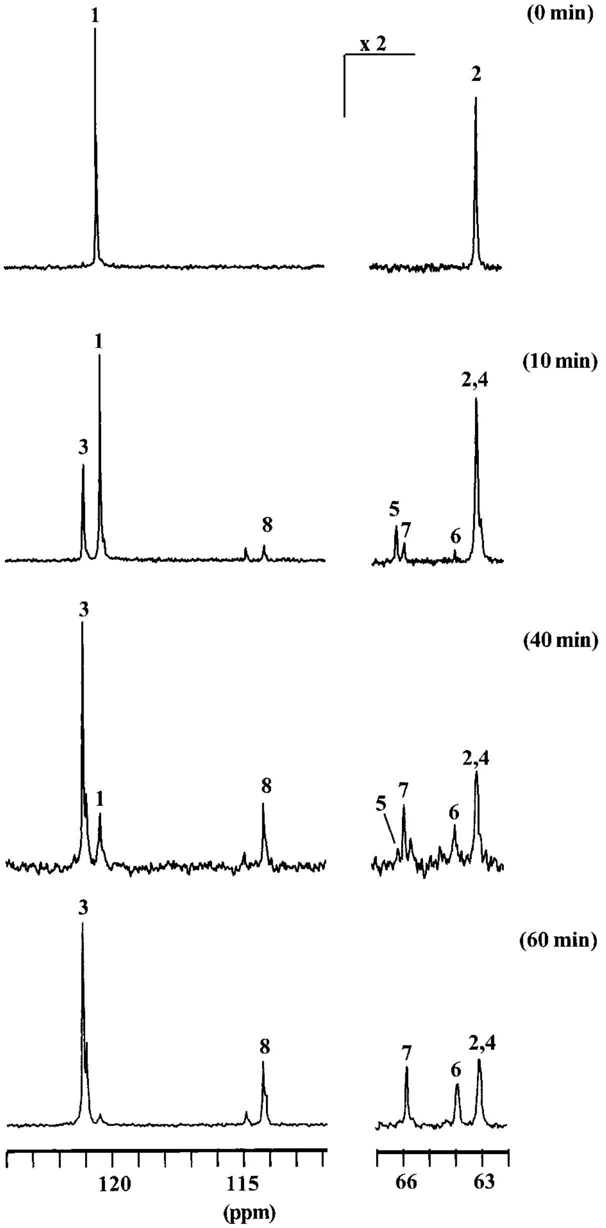


Figure 5. ^{13}C NMR spectra of 50:50 (w/w) PC/PET blend melt-mixed at 270 °C for 0, 10, 40, and 60 min in the presence of catalyst. The carbon assignments are given in Scheme 2.

4). The presence of a shoulder at 4.3 ppm due to butylcarbonate units, i.e., the linking units of PC/PBT copolymer, is also observed.

The data relative to the material balance of the reactions of PC with the three samples of OH-terminated PBT, obtained by selective extraction and by ^{1}H NMR, is reported in Table 2. It can be noted that the amount and the composition of the copolymers generated in these reactions are constant as a function of the time (Figure 2). The weight of copolymer formed in the reaction increases with the molar mass of the PBT used (Figure 2a), whereas the copolymer composition shows an excess of PBT units with respect to the feed molar ratio (Figure 2b), as predicted for this case (Table 1).

A remarkable difference with the analogous case of the PET/PEA ester–ester exchange described earlier[22] is that in the case of ester–carbonate exchange the reactive hydroxyl groups are consumed in the reaction (because unreactive phenoxy groups are generated,

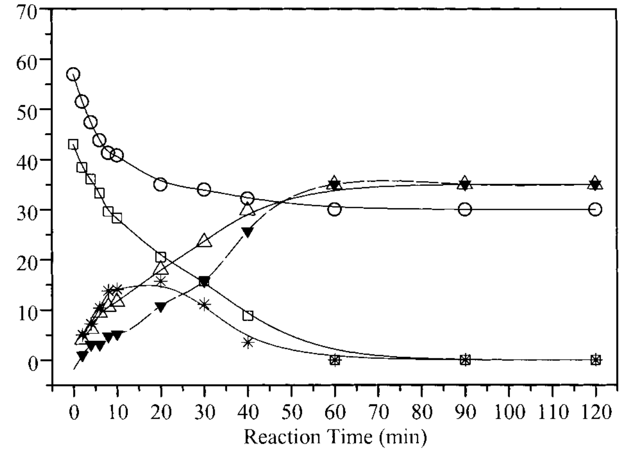


Figure 6. Amount (mol %) of structural units in the copolymer as a function of the reaction time for (□) A, (○) B, (△) C, (*) D, and (▼) E. (Structural units are indicated in Scheme 2.)

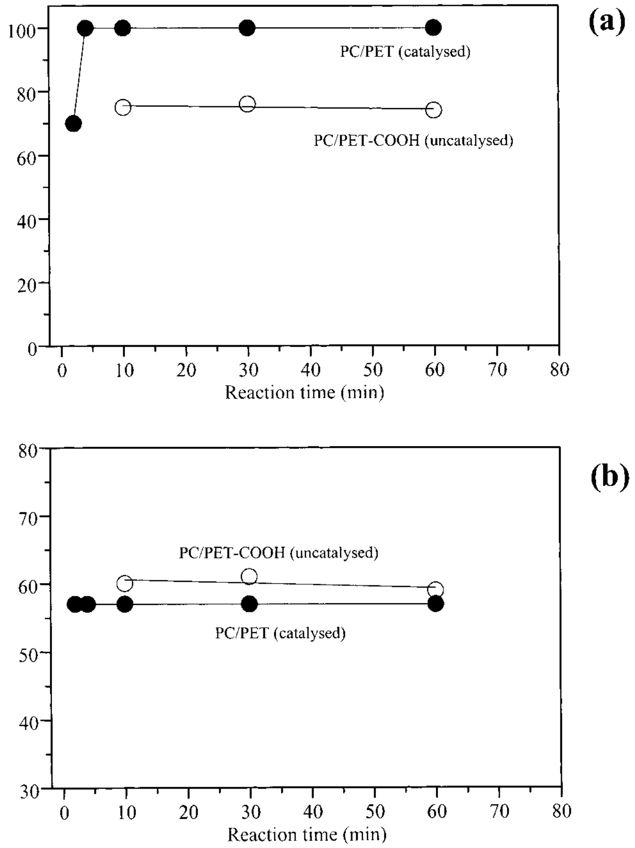


Figure 7. (a) Weight percent and (b) composition of the copolymer produced in the melt-mixing at 270 °C of (●) catalyzed PC/PET blend, and (○) uncatalyzed blend of carboxyl terminated PET with PC.

Scheme 1b, Table 1), whereas in the PET/PEA system the reactive hydroxyl groups are continuously regenerated and the composition of the copolymer shows an excess of PEA units at the beginning of reaction, which then equilibrates and comes close to the feed molar ratio of the homopolymers, in the later stages of the reaction.[22,23]

PET/PC BLENDS. As in the case of PBT/PC blend, to correlate the composition of the copolymers to the exchange mechanisms we have reacted at 270 °C a 50:50 (w/w), high molar mass PC and PET sample in the presence of $Ti(OBut)_4$ and a 50:50 (mol/mol) blend of PC

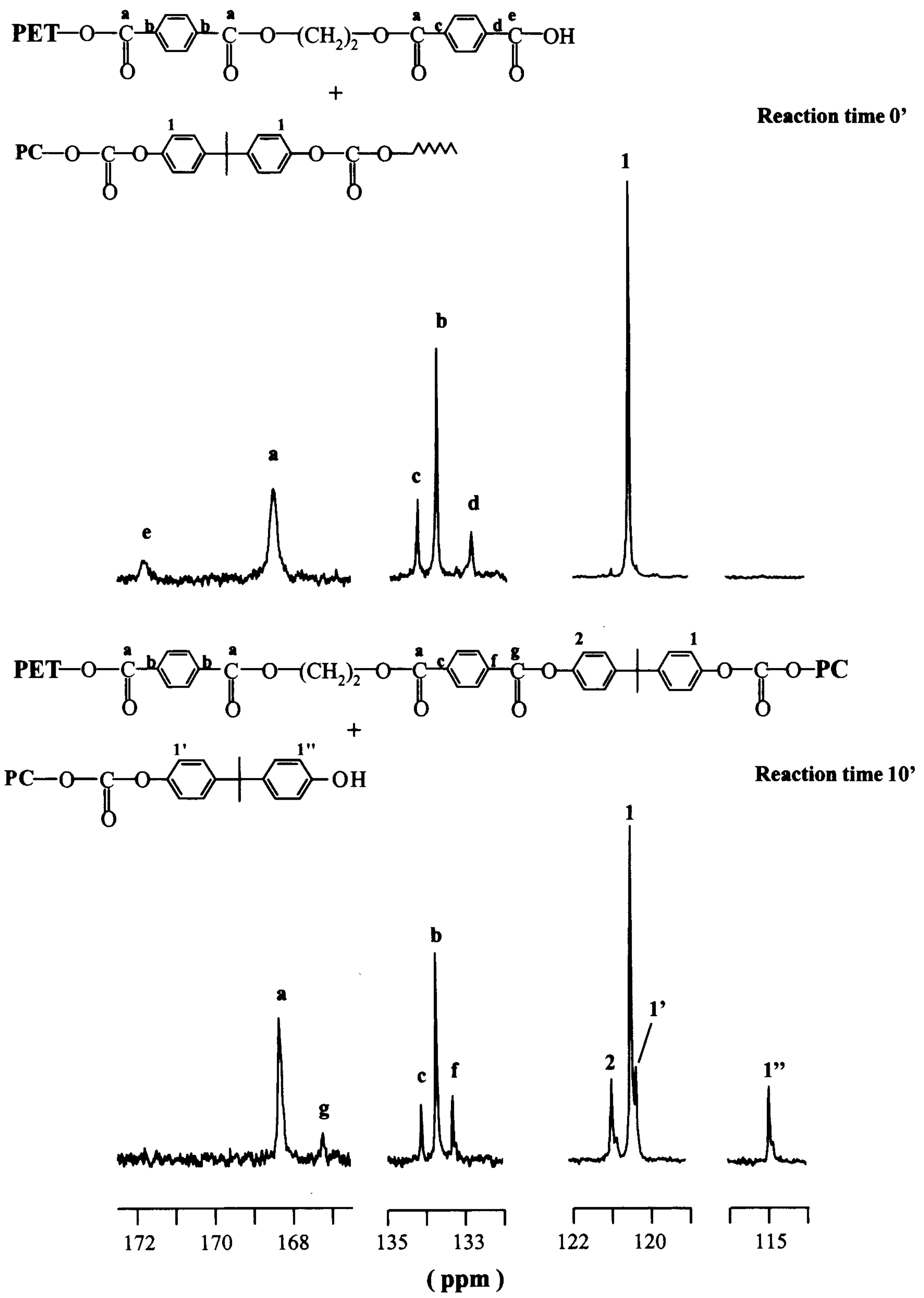


Figure 8. ^{13}C NMR spectra of uncatalyzed blend of carboxyl-terminated PET with PC melt mixed at 270 °C for 0 and 10 min.

with COOH-terminated PET sample as a function of reaction time.

The catalyzed exchange reaction of high molar mass PET and PC is likely to occur by an inner–inner exchange mechanism analogous to the PBT/PC system generating a four-component copolymer (A, B, C, D, Scheme 2). However, at this temperature (270 °C) the aliphatic carbonate units formed in the exchange undergo thermal decomposition by the elimination of CO_2 and ethylene carbonate (ETC), simultaneously to the exchange reaction. The elimination of CO_2 causes the formation of ether groups along the copolymer chain, therefore introducing a new component into the copolymer sequence (E, Scheme 2).[10–13]

The exchange reaction was monitored by ^{13}C NMR following the intensity changes of signals corresponding to methylene (62−66 ppm) and to Bisphenol A (114−121 ppm) (see Scheme 2 for the assignments) as a function of time (Figure 5). The spectra of four PET/PC samples reacted for 0, 10, 40 and 60 min show the presence of the following: peaks **1** and **2** at 120.3 and 62.96 ppm corresponding to the copolymer sequences A and B (Scheme 2), respectively; peaks **3** and **5** at 121 and 66 ppm assigned to C and D sequences; peaks **6**, **7**, and **8** at 63.9, 65.8, and 114 ppm due to ether units (E sequence, Scheme 2).

The material balance of the reaction, obtained by ^{1}H NMR and ^{13}C NMR, is reported in Table 3 and shows that after 2 min of reaction the copolymer is essentially constituted of a four-component copolymer (A, B, C, D, Scheme 2), that become five components from 4 min up to 40 min. After this time the A and D carbonate sequences are totally consumed by the elimination of CO_2 and ethylene carbonate, and a three-component copolymer (B, C, E) is produced (Figure 6).

The weight of copolymer formed after 2 min of mixing is 70%, and the reaction goes to completion after 4 min (Table 3, Figure 7a).

The weight loss of ETC and CO_2, calculated by NMR (see Experimental Section), is in agreement with the weight loss data obtained by isothermal thermogravimetric analysis at 270 °C of a PET/PC sample in the presence of catalyst (Table 3). This fact indicates that the weight loss detected by NMR, actually coincides with the total loss of material occurring in the system.

The composition of the copolymer obtained in the catalyzed reactive blending of the PET/PC system is reported as a function of reaction time in Figure 7b. It can be noted that the molar amount of the terephthalate units in the extracted copolymers is 57%, i.e., identical to the feed composition, and it remains constant with the reaction time, as predicted (Table 1).

As in the case of the PBT/PC system (reactions b and c of Schemes 1), the uncatalyzed exchange reaction of high molar mass PC with a PET sample containing carboxyl end groups is likely to occur by an outer−inner mechanism (Figure 1d), and it does not need the presence of catalysts.

The reaction was performed at 270 °C and was monitored by ^{13}C NMR following some pertinent peaks as shown in Figure 8. It can be observed that peaks **e** and **d** at 171.3 and 132.7 ppm corresponding to carbonyl and to quaternary carbons of terephthalate carboxyl end groups disappear after 10 min of reaction and are substituted by the peaks **g** and **f** at 167 and 133 ppm corresponding to carbonyl and to quaternary carbon of aromatic terephthalate units, which are generated during the exchange reaction and constitute the linking units of PET and PC blocks in the copolymer. Peak **2** at 121 ppm is assigned to the Bisphenol A tertiary carbon of the aromatic terephthalate units. Peaks **1′** and **1″** at 120.2 and 115 ppm can be assigned to tertiary carbons of BPA units bearing hydroxyl end groups. The latter are generated by the decomposition of carbonate end groups (Scheme 1c). The phenol terminal groups of PC are unreactive and the exchange reaction stops as soon as the carboxyl reactive groups are consumed.

As in the case of the PBT/PC system, the weight of copolymer formed remains constant with the reaction time (about 75%, Figure 7a). The composition of the copolymer formed is also constant (Figure 7b) and shows an excess of PET units (60% against a molar feed ratio of 50%). This result is in agreement with the predictions made in the introductory section and with the results obtained with PBT-containing hydroxyl groups.

Conclusions

BPA−polycarbonate is easily attacked, in the molten state, by the reactive end groups of PET or PBT. The mechanism of these reactions is different from the ester exchange between inner groups occurring in the catalyzed reaction.

The presence of alcoholic or carboxylic end groups in the melt mixing process with PC may cause “inner−outer” reactions which influence the yield and composition of the copolymers obtained. Therefore, the content of end groups should be controlled in order to avoid composition fluctuations in these processes.

To predict the behavior of these systems, a simple approach has been introduced here.

Inner−inner and inner-outer mechanisms operating in the exchange reactions occurring in the melt mixing processes of PBT/PC and PET/PC systems have been investigated making use of appropriate polymers, end capped or containing active chain end groups.

Monitoring the composition of the copolymer formed in each case proved to be a diagnostic tool for establishing the mechanism of reaction.

The results obtained fit reasonably well with those reported previously in the study of ester−ester exchange.[22]

The diagnostic approach used here allows control of the composition and yield of the copolymer to be produced, and it is applicable to other systems where exchange reactions occur.

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