Chemical Modification of Bisphenol A Polycarbonate by Reactive Blending with Ethylene Carbonate

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ABSTRACT: A new method for the insertion of aliphatic moieties into bisphenol A (BPA) polycarbonate (PC) by reactive blending with ethylene carbonate (ETC) has been developed. By this route, new polymeric materials with modified thermal and rheological properties have been synthesized; the structure of the poly(ether-co-carbonate)s prepared can be controlled using different ETC/PC molar ratios. Using model compounds and selective degradation reactions, the different chemical structures of the aliphatic units inserted into PC backbone were identified. ETC/PC molar ratios below 1 afforded both aliphatic–aromatic carbonate and ether groups, while higher ETC/PC molar ratios afforded aliphatic–aromatic ether and aliphatic–aliphatic carbonate groups. The co-polymers prepared by the new process were clear without discoloration or opacity. The thermal analyses of the co-polymers showed that, by the insertion of aliphatic moieties, it is possible to modulate the glass transition temperature (T_g) in a 30°C range. A decreased melt viscosity of the co-polymers was also observed and therefore an improved processability should be expected with respect to standard PC. The reaction with aliphatic carbonates can be also considered as a promising chemical recycling process for PC scraps, through the synthesis of monomers such as bis(hydroxyethyl)ether of BPA. This monomer has already been used for the preparation of co-polyesters of terephthalic acid with high T_g and thermal stability. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 2014, 131, 39820.

INTRODUCTION

Aromatic polycarbonates (PCs), and in particular bisphenol A (BPA) PC, constitute a widely used and versatile class of engineering thermoplastics[1–6]; for them a continuous dynamic growth is expected in the next few years.[1] The main reasons for this outstanding performance depend not only on their unique combination of useful properties and excellent price/performance balance, but also on the intrinsic capability of the PC structure to be easily and widely modified.[7] For example, new polymeric materials such as statistical and block co-PC (e.g., polyether-co-carbonates[8] and polyester-co-carbonates[9,10] can be obtained by incorporation of alternative monomers.

PC is often modified in order to change its rheological properties, for example by insertion of branching agents (e.g., tri- or poly-functional monomers[11], variation of end-groups,[12] and by insertion of aliphatic moieties.[13–18] The insertion of aliphatic moieties is industrially used[18] in order to reduce the glass transition temperature (T_g) and to obtain polymers with higher melt flow rate. Indeed, a lower T_g leads to a melt viscosity reduction and therefore to a better processing of the material. Other routes to prepare PC grades with improved melt flow

properties have been reported in the literature[19–22]; for example, blending PC with oligomers[19] or other polymers such as acrylonitrile butadiene styrene (ABS),[20] polyesters,[21] or polydimethylsiloxane[22] yields polymer blends with better flow and processing properties. However, the resulting materials are not completely transparent, thus preventing their use in applications that demand light transmission or clarity.[18]

Recently, a new class of PC copolymers composed of BPA and a bio-sourced co-monomer, derived from castor bean oil, has been introduced to the market by SABIC-IP under the trade name Lexan HFD (High Flow Ductile).[18,23] The method reported[13–17] are performed during the interfacial polymerization process of PC and requires the use of α-ω aliphatic dicarboxylic acids or acid chlorides containing, usually, 6–20 methylene units.

On the light of the increasing importance of the melt polymerization process[1,2,24] for the synthesis of BPA PC, since it does not require the direct use of phosgene, we have carried out studies regarding the exchange reactions of polycondensation polymers with cyclic carbonates and anhydrides.[25–27]

Ethylene carbonate is an important cyclic carbonate and can be used as intermediate or reagent to produce PC by phosgene free routes.[28–30] For example, in the Ashai phosgene free process,[29,30] ethylene carbonate (ETC) can be used for the production of methyl carbonate, an intermediate in the production of diphenyl carbonate (DPC) (the monomer used for the melt polymerization process of PC). Another important feature of ETC is that it can be obtained from renewable resources.[31]

The reaction of ETC with PC has been previously reported in a patent for the preparation of poly(ether-co-carbonate)s.[32] The reactions were carried out at very high temperatures (exceeding 280°C) and for long reaction times. However, the exact chemical composition of the polymers obtained, their glass transition temperature, and the reaction mechanism have not been reported.

The use of ETC in combination with ethylene glycol has been reported by Oku et al.[33] with the aim to chemically recycle PC. Using this method, PC was partially converted into the bis(hydroxyethyl) ether of bisphenol A (BHEEB). Indeed, ethoxylated bisphenol groups are interesting monomers that can be used for the preparation of terephthalate polyesters co-polymers with increased glass transition temperature and thermal stability with respect to standard terephthalate polyesters.[34–38] For all these reasons, it is clear the importance to study in detail the chemical composition and the mechanism of the reaction of ETC with PC, both for the preparation of polymers with high melt flow and for the chemical recycle of PC. To the best of our knowledge, nobody has ever reported the complete chemical characterization and the thermal properties of copolymers obtained by the reaction of PC with ETC. Therefore, in this article, we describe the preparation of PC copolymer with low T_g and melt viscosity by reactive blending of PC with ETC, also reporting a detailed study of the reaction mechanism, the determination of the chemical structure of the polymers obtained with different ETC/PC ratios, as well as their thermal properties.

EXPERIMENTAL

DPC, ethylene carbonate, sodium phenoxide (SPO), and dibutyl tin dimethoxide (DBTM) (all from Aldrich) (all with purities declared from the manufacturer of 99% or more) were not purified before use. Titanium tetrabutoxide (TBT) (from Aldrich) was distilled in vacuum before use. Poly [2,2-bis(1,4-phenylene)propane carbonate] (BPA PC) from Enichem (M_w 43,500, T_g = 154°C) was dried overnight at 130°C under reduced pressure before use.

Model Compound Reactions

Diphenyl Carbonate/Ethylene Carbonate Reactions. DPC (42.8 g, 200 mmol) and ETC (38.8 g, 400 mmol) were placed in a 250-mL round-bottom flask provided with a water-cooled condenser. The reaction was conducted at 245°C for 2 h under magnetic stirring. A strong effervescence was observed when the reaction temperature exceeded 200°C. After 2 h, the effervescence ended and the reaction mixture was cooled and washed with hot methanol. The crude product was analyzed by ^{1}H-NMR and by gas chromatography (GC).

The reaction was repeated with an ETC/DPC molar ratio of 1 : 4, in the presence of 0.088% by moles (respect to DPC) of SPO as catalyst. The reaction with ETC/DPC molar ratio of 2 was also conducted in the presence of Lewis acid catalysts (TBT and DBTM 0.088% by moles respect to DPC). In this case no effervescence occurred.

The reaction products were separated by chromatography on a silica-gel column using a chloroform/methanol mixture (4/1 vol/vol) as eluent. The analysis of the different fractions was performed by ^{1}H-NMR spectroscopy and mass spectroscopy.

^{1}H-NMR (solvent CDCl$_3$) of ETC/DPC (1/1 molar ratio) main reaction product (65% by mol): δ(ppm downfield from TMS) 7.50–6.95 (10H; m); 4.65 and 4.25 (4H; AB system composed of two triplets).

^{1}H-NMR (solvent CDCl$_3$) of ETC/DPC (2/1 molar ratio) reaction product: δ(ppm downfield from TMS)7.35–7.25 (4H; m); 7.05–6.90 (6H; m); 4.55 and 4.15 (8H; AB system composed of two triplets).

Sodium Phenoxide/Ethylene Carbonate Reactions. SPO (3.00 g, 26.0 mmol) and ETC (2.28 g, 26.0 mmol) were placed in a 50-mL round-bottom flask. The temperature of the silicon oil bath was then increased from room temperature to 200°C and the reaction kept at this temperature for 30 min. The flask was taken out from the oil bath, cooled to room temperature, and the reaction mixture was quenched with water.

The reaction mixture was separated by chromatography on a silica-gel column using a chloroform/methanol mixture (9/1 vol/vol) as eluent. The only reaction product was 2-phenoxy ethanol (yield 75%) (m/z = 138 by mass spectrometry analysis). ^{1}H-NMR (solvent CDCl$_3$) of the main product: δ(ppm downfield from TMS)7.20–7.10 (2H; m); 6.85–6.70 (3H; m); 4.10–3.95 (4H; AB system composed of two triplets).

ETC/PC Reactions

Bisphenol A Polycarbonate/Ethylene Carbonate Reactions in Glass Reactor. PC (10.2 g, 40.0 mmol of repeating unit) and ETC (7.04 g, 80.0 mmol) were placed in a 100-mL round-bottom flask provided with a water-cooled condenser. The reaction was conducted at 245°C for 2 h. A strong effervescence was observed when the reaction temperature exceeded 200°C. After 2 h, the effervescence was over. The reaction mixture was cooled to room temperature and the polymer was dissolved in CH$_2$Cl$_2$, precipitated in methanol and dried overnight at 60°C under vacuum.

This reaction was repeated using an ETC/PC molar ratio of 0.5, 1, 2, and 4 (respect to the repeating unit of PC). In the presence of the catalyst (SPO, 0.088% by mol respect to PC repeating unit), the effervescence was over after 10 min. In all the cases, the final polymers did not show any discoloration. The reaction crude products were analyzed by ^{1}H-NMR spectroscopy and gel permeation chromatography (GPC); the results are reported in the results and discussion section.

The reaction with ETC/PC molar ratio of 2 was also conducted in the presence of Lewis acid catalysts (TBT and DBTM 0.088% by mol respect to PC repeating unit). In these cases, almost no
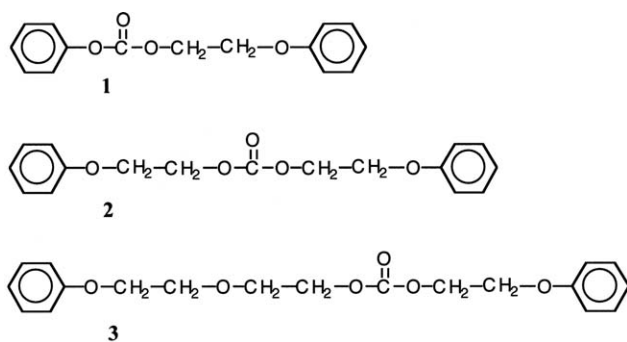
Figure 1. Products of the reaction between DPC and ETC.

effervescence occurred and a strong discoloration of the final polymers was observed. The polymer structures were analyzed by ^{1}H-NMR and the molecular weights were measured by GPC using chloroform as eluent. The results are reported in the results and discussion section.

Bisphenol A Polycarbonate/Ethylene Carbonate Reactions in Brabender Plasticorder Mixer. The reactions were performed in a Brabender Plasticorder PL2000/W50 with an ETC/PC molar ratio (based on the PC repeating unit) ranging from 0.05 to 0.5. ETC was added to 40.0 g of PC at 225°C. After 2 min the catalyst (SPO, 0.022% by mol respect to PC repeating unit) was added and the temperature was increased to 245°C. The reaction was stopped after 30 min and the polymer recovered from the Brabender mixer.

Selective Degradation Reactions
A suspension of 2.00 g of precipitated and dried polymer in 50 mL of a KOH solution (1N) in methanol was stirred for 10 h at 80°C. The white suspension was then neutralized with HCl 37% (wt/wt) and the solvent evaporated under reduced pressure. The white solid was extracted three times with hot chloroform. The chloroform was then evaporated under reduced pressure, affording a pale yellow solid. The degradation products were then separated by chromatography on a silica-gel column using a chloroform/methanol mixture (4/1 vol/vol) as eluent. The analysis of the different fractions was performed by ^{1}H-NMR spectroscopy and GC.

Instrumental
DSC Analysis. The DSC analyses were performed on a Perkin Elmer DSC7. The sample (ca., 5 mg) was heated from room temperature to 200°C at 20 °C/min (1st scan) and then rapidly quenched to room temperature. The sample was then reheated to 200°C at 20 °C/min (2nd scan). The glass transition temperatures have been measured on the second scan in order to erase the previous thermal history and provide the same heat treatment to all samples. T_g values were taken as the midpoint of the heat capacity increment (ΔC_p) associated with the glass transition.

Thermo-gravimetric Analysis. The thermo-gravimetric curves were obtained in air using a Perkin Elmer TGA7 apparatus (gas flow: 50 mL/min) with a 10 °C/min heating rate from 25°C to 900°C.

Thermal Stability Analysis in Glass Tube. About 1.00 g of polymer was placed in a glass tube (height 15 cm; internal

diameter 3 cm) provided with a stopcock. The air inside the glass tube was removed by applying vacuum for 2 min. The stopcock was then closed and the glass tube immersed into a silicon oil bath electrically heated at 300°C. After 30 min, the glass tube was extracted from the oil bath and cooled to room temperature. The polymer was analyzed by GPC using CHCl$_3$ as eluent.

Gel Permeation Chromatography. The GPC measurements were performed on a Agilent series 1100 HPLC equipped with a PL gel 5 μ mixed C column with CHCl$_3$ as eluent. An UV detector set at 254 nm was used. The solution injected had a concentration of 0.1 wt %. The molecular weights were determined using a calibration curve obtained from polystyrene standards.

^{1}H-NMR. ^{1}H-NMR spectra were recorded using a Varian XL-300 spectrometer (chemical shifts are downfield from TMS). CDCl$_3$ was used as solvent.

Mass Analysis. Mass spectra were obtained using electron impact (70 eV) in a VG7070 mass spectrometer.

Gas Chromatography. GC analyses were performed using a Agilent GC 6890 series with auto-sampler, using a 30 m (ID 0.53 mm, film thickness 1.2 μ) Alltech EC-Wax (Carbowax) column. A flame ionization detector (FID) was used.

RESULTS AND DISCUSSION

Due to the complexity of the reactions occurring in reactive blending of PC with ETC, model compounds were used in order to identify the chemical structure of the final products and to investigate the mechanism of the reactions. The knowledge of the reaction mechanism may help to design proper reaction conditions that allow the synthesis of polymers with the desired chemical structure. In addition, it may be applied to the development of other processes, such as for example, the phosgene free synthesis of PC using ETC.[28–30]

Model Compounds Reactions
The first set of experiments has been performed using model compounds in order to identify the products of the reaction between PC and ETC and to provide an insight on the reaction mechanism. DPC was used as a model compound for PC. The reactions between DPC and ETC, in different molar ratios, were conducted at 245°C in a glass reactor without catalyst or in the presence of a basic catalyst (SPO) or a Lewis acid catalyst (titanium butoxide or DBTM). The reaction products were separated by column chromatography. The ^{1}H-NMR analysis of each fraction showed that the chemical structure of the products strongly depends on the ETC/DPC ratio and on the nature of the catalyst used. In all the cases, the main reaction products were among the three compounds reported in Figure 1.

The composition of the product mixtures obtained using different ETC/PC molar ratio and catalysts is reported in Table I. Using an ETC/DPC molar ratio of 1 and SPO as catalyst, the main component was phenyl 2-phenoxyethyl carbonate (**1**), with 12% by mol of bis(2-phenoxyethyl) carbonate (**2**) and unreacted DPC as minor components. On the contrary, only product **2** was obtained using an ETC/DPC molar ratio of 2. Increasing the ETC/DPC molar ratio to 4, the main product

Table I. Reaction Products Formed During ETC/DPC Model Reactions

ETC/DPC	Catalyst	Ureacted ETC (mol %)	Product **1** (mol %)	Product **2** (mol %)	Product **3** (mol %)
0.5	SPO	15	85	0	0
1	SPO	10	65	12	0
2	SPO	0	0	99	0
4	SPO	0	0	65	20
2	–	96	4	0	0
2	TBT	96	2	0	0
2	DBTM	98	2	0	0

was again **2**, but the product mixture contained also 20% by mol of 2-phenoxyethyl 2-(2-phenoxy ethoxy)ethyl carbonate (**3**).

Using Lewis acid catalysts such as TBT and DBTM, two well-known catalysts for exchange reactions,[39–41] a very low conversion of the reagents was obtained, since the reaction mixture was mainly composed of unreacted DPC and ETC. A small amount (2% by mol) of ethylene glycol bis(phenyl carbonate) was also present in the reaction mixture. A very low conversion was also observed in the absence of catalysts.

The chemical structure of the reaction products **1**, **2**, and **3** indicates that the mechanism evolves via a selective decarboxylation of the anion of the carbonic acid monoester. This anion is formed by nucleophilic attack of the phenoxide ion on ETC. It is reported in the literature[42,43] that nucleophilic reagents can attack ethylene carbonate both at the methylene group and at the carbonyl moiety. The two possible reaction pathways are represented in Figure 2. A reaction between ETC and SPO in equimolar amounts was conducted at 200°C for 30 min in order to verify the position of attack of the SPO on ETC.

The reaction mixture, after quenching with water, was separated by column chromatography. The only product (75% yield) was characterized by ^{1}H-NMR and mass spectroscopy and was identified as 2-phenoxyethanol. For this reason it is possible to assume that in this case the phenoxide ion attacks only the methylene moiety of ETC (path **b** in Figure 2).

On the basis of the results obtained from the ETC/DPC and the SPO/ETC model reactions, the mechanism in Scheme 1 was proposed for the base catalyzed reaction. In the first step, the basic catalyst attacks the methylene group of ETC leading to the formation of intermediate **4**, bearing the anion of a carbonic acid monoester. This group is unstable at the reaction temperature and, by decarboxylation reaction, it is converted into

intermediate **5**, an alkoxide containing an aliphatic–aromatic ether linkage. This alkoxide can attack the carbonate group of DPC leading to **1**, which is the main product obtained when employing an ETC/DPC ratio of 1 or lower. Intermediate **5** can also react with the carbonyl of **1**, leading to **2**.

Not only can the alkoxide **5** react with carbonate groups, but it can also react with the methylene group of ETC leading to aliphatic–aliphatic ether linkages. Nevertheless, the reactivity of the alkoxide **5** with ETC is lower than its reactivity with aromatic–aromatic carbonate groups. Indeed, we observed the formation of aliphatic–aliphatic ether linkages only for ETC/DPC molar ratios higher than 2. The formation of **3** can be explained by the reaction of intermediate **5** with ETC, which leads to intermediate **6**, which then loses CO_2 to give intermediate **7**. Intermediate **7** can attack the carbonyl of **2** affording **3**.

ETC/PC Reactions

The ETC/PC reactions were first performed in a glass reactor at 245°C, in the presence of 0.088% by mol (with respect to PC repeating unit) of SPO as catalyst. After 2 min of reaction a strong effervescence, due to CO_2 production, was observed. All the polymers obtained were transparent without any discoloration or haze. The ^{1}H-NMR spectra of the polymers obtained using ETC/PC molar ratios of 0.5, 1, 2, and 4 are reported in Figure 3 together with the spectrum of the starting PC.

The NMR spectrum with an ETC/PC molar ratio of 2 indicates the formation of aliphatic–aromatic ether and of aliphatic–aliphatic carbonate linkages, since it presents two AB systems, one at 7.10 and 6.80 ppm and one at 4.50 and 4.15 ppm. According to model compound reactions and to the intensity of the integrals of the two AB systems, structure **B** in Scheme 2 can be clearly identified. It has two ethylene groups linked by a carbonate moiety and joined to BPA by ether linkages. No signal due to unreacted carbonate groups of starting PC has been observed in this case.
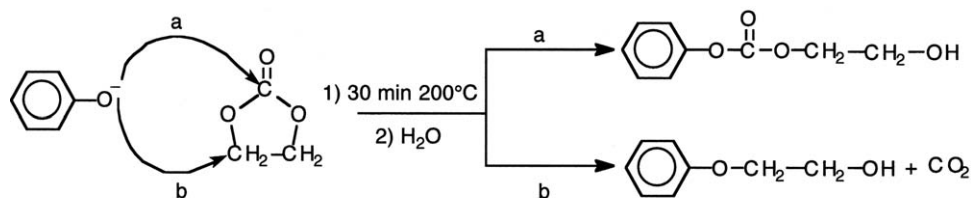
Figure 2. Possible paths of the reaction between SPO and ETC.
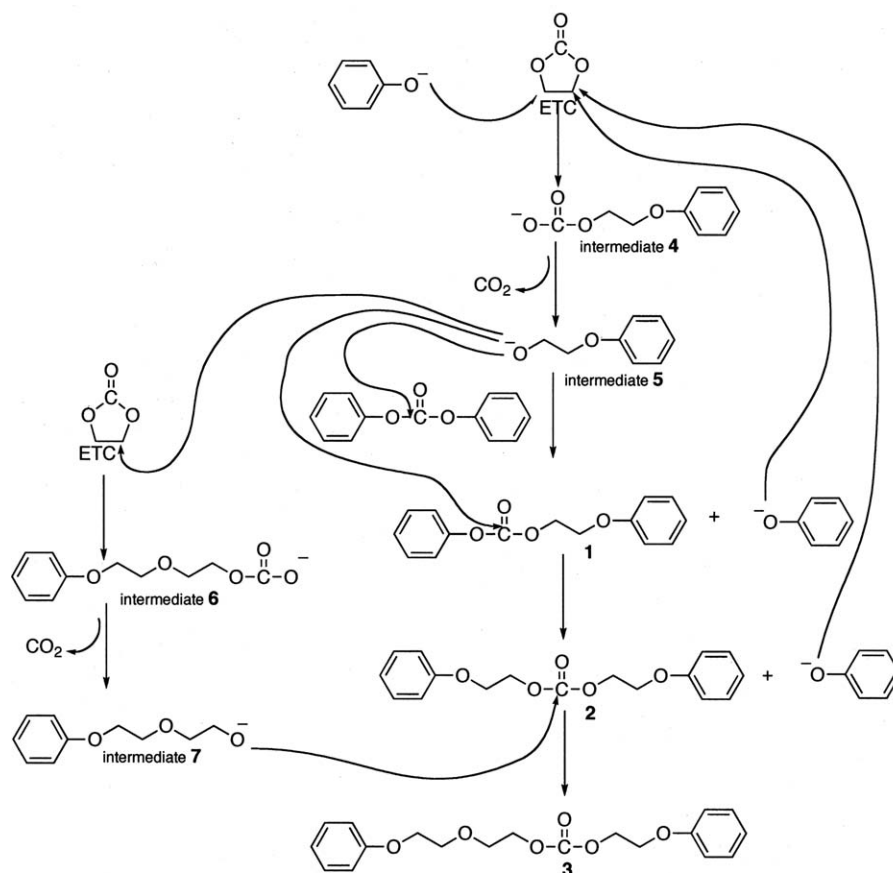
Scheme 1. Mechanism of the model reaction of ETC with DPC catalyzed by SPO.

The polymer prepared with an ETC/PC molar ratio of 2 was degraded by reacting it with a KOH solution (1N) in methanol. By this method it was possible to selectively cleave the carbonate moieties into two alcoholic groups, leaving the ether linkages unaffected. The degradation afforded in this case 99% by mol of BHEEB, confirming the formation of structural unit **B**. Therefore, this polymer and this degradation reaction can been used for the chemical recycle of PC, since the insertion of BHEEB groups has been proved to be an efficient method to increase the glass transition temperature of terephthalate polyesters.[34–38]

The formation of structure **A** in Scheme 2 is confirmed by the NMR analysis of the reaction product obtained with an ETC/PC ratio of 0.5. Indeed, the ^{1}H-NMR spectrum presents an AB system at 4.65 and 4.25 ppm that, in accordance with model compounds, indicates the formation of aliphatic–aromatic carbonate groups. The selective degradation in KOH and the analysis of the degradation products by ^{1}H-NMR and GC also indicates the formation of structure **A**. Peaks assigned to structures **A** and **B** are present in the NMR spectrum of the reaction products with an ETC/PC molar ratio 1.

The spectrum obtained using an ETC/PC molar ratio of 4 presents, in addition to the peaks characteristic of structure **B**, three multiplets at 3.70, 4.15, and 4.30 ppm that indicates the presence of aliphatic–aliphatic ether moieties. This is in agreement with the results of the GC and NMR analysis of the

products of the selective degradation reaction that showed the presence of aliphatic–aliphatic ether linkages.

A summary of the results of ETC/PC reactions is presented in Table II. The relative amount of structures **A** and **B** was determined by ^{1}H-NMR. In particular, the amount of ETC inserted was measured comparing the intensity of the two AB systems at 4.65–4.10 ppm due to structures **A** and **B** with the total intensity of aromatic signals (7.40–6.70 ppm). The amount of unreacted ETC was measured by comparing the intensity of the integral assigned to the singlet of ETC at 4.55 ppm with the total intensity of aromatic peaks.

As expected on the basis of model compound reactions, Lewis acids do not catalyze the reaction since only less than 2% by mol of ETC had reacted after 2 h at 245°C in the presence of titanium or tin-based catalysts.

The results in Table II also show that basic catalysts led to a small molecular weight decrease. On the contrary, Lewis acid catalysts produced a consistent molecular weight decrease and a significant discoloration of the final products. When no catalyst was added, the molecular weight of the polymers after the reaction was identical to that of the starting PC.

The reaction has then been performed using different SPO levels (with a ETC/PC molar ratio of 0.5) in order to detect the effect of the catalyst content on the reaction rate and molecular weight (Table III). Shorter reaction times are required to reach high conversions using the higher catalyst contents.
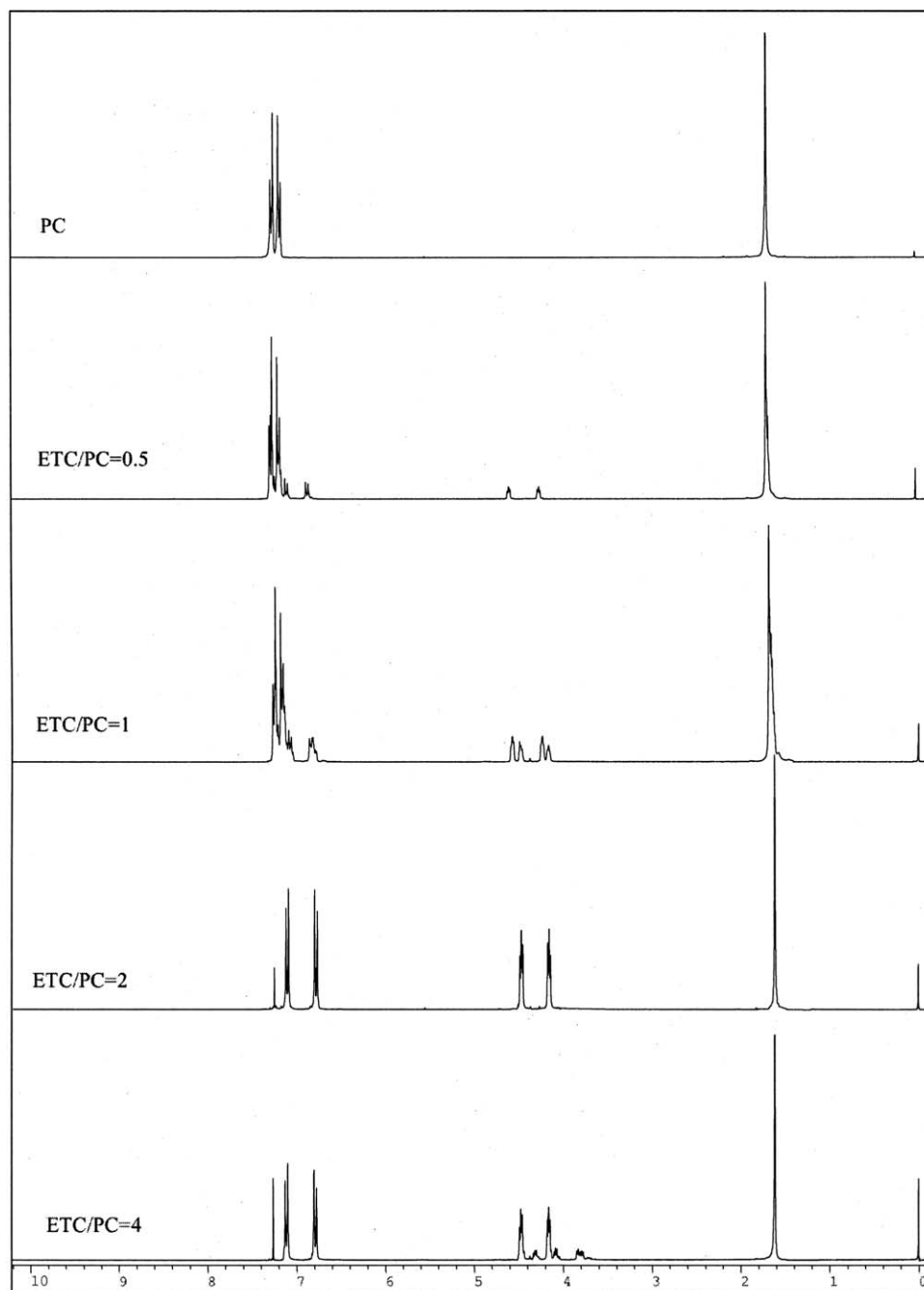
Figure 3. ^{1}H-NMR spectra of polymers obtained using ETC/PC ratios of 0.5, 1, 2, and 4.

Nevertheless, even if the reactions were faster, lower molecular weight polymers were obtained with the higher catalyst contents. Indeed, the reaction of SPO with PC causes a scission of the polymer chain, leading to lower molecular weight products.

The reaction was then carried out sampling the reaction melt in order to measure the composition of the different products during the reaction. This experiment was performed in order to evaluate the possibility to selectively obtain polymers with only **A** or **B** structures. The reaction was conducted using an ETC/PC molar ratio of 2, in the presence of SPO (0.022% respect to PC repeating unit) as catalyst, taking samples from the melt every 5 min. The

amount of the different species in the melt was evaluated by ^{1}H-NMR analysis (Figure 4). It is worth noting that structure **A** is formed first and then reacts to form structure **B**. Therefore, its concentration goes through a maximum after 50 min and then decreases to 0 after 120 min, when only structure **B** is present. This indicates that if only structure **A** is aimed at, a low amount of ETC (less than 0.5) must be used.

Reaction Mechanism

On the basis of the mechanism of model compound reactions, of the ^{1}H-NMR spectra in Figure 3 and of the results of the degradation reactions, the mechanism in Scheme 2 can be
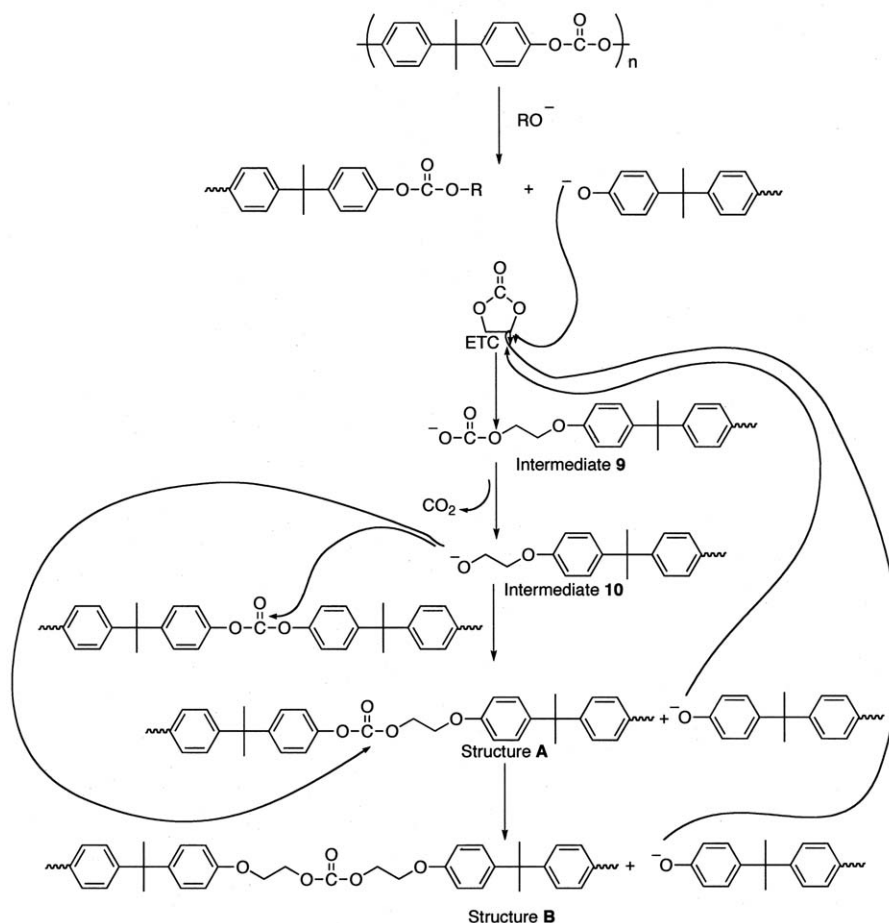
Scheme 2. Mechanism of the reaction of ETC with PC catalyzed by SPO.

proposed for ETC/PC base catalyzed reactions. As observed in model compound reactions, the reaction evolves through the formation of phenoxide end-groups that react with methylene groups of ETC, leading to the formation of intermediate **9**. The latter affords alkoxide end-groups (**10**) by CO_2 elimination. The alkoxide (**10**) can react with the carbonate moieties of PC leading to structure **A** that contains an aliphatic–aromatic carbonate and an aliphatic–aromatic ether linkage. Again, the alkoxide end-group can react with structure **A** leading to structure **B**.

Thermal Properties of the Copolymers

Since it is well known that aliphatic–aliphatic and aliphatic–aromatic carbonates are less stable to thermal degradation with respect to fully aromatic carbonates,[1] the thermal stability of the co-polymers obtained by reaction of PC with ETC was studied by thermo-gravimetric analysis (TGA). The TGA curves of polymers containing 6% and 25% of structure **A** and 99% of structure **B** are presented in Figure 5. The TGA curve of PC is also included as reference.

Table II. Results of ETC/PC Reactive Blending in Glass Apparatus Performed at 245°C (Catalyst Level 0.088 mol % with Respect to PC Repeating Unit)

| ETC/PC	Catalyst	Reaction time (min)	ETC inserted Bisphenol groups	ETC unreacted Bisphenol	Structural unit A (A+B)	Structural unit B (A+B)	M_w GPC
0.5	SPO	10	0.49	0	0.85	0.15	39,800
1	SPO	10	0.98	0	0.74	0.26	38,900
2	SPO	10	2.00	0	0	1.00	34,500
4	SPO	10	4.00	0	0	0.60	31,000
2	–	120	0.05	1.81	1.00	0	43,500
2	TBT	120	0.03	1.79	1.00	0	8700
2	DBTM	120	0.04	1.85	1.00	0	15,200

Table III. Effect of Catalyst Content on Reaction Time and Molecular Weight

Catalyst content (mol % respect to PC) content	Reaction time (min)	Molecular weight
0.022	30	41,500
0.088	10	39,500
0.176	5	34,500

Figure 5. TGA analysis of polymers obtained by ETC/PC reactive blending with 0.088 mol % of SPO as catalyst.

TGA analysis results show that increasing the aliphatic unit content in the polymer chain decreases the thermal stability and increases the weight loss in the first degradation step. Nevertheless, with aliphatic units content lower than 25% by mol, no weight loss was observed below 390°C. A higher thermal stability was observed for the polymers obtained with lower SPO amounts. In particular, the 5% loss temperature was 25°C higher for the polymer obtained using 0.022% of SPO with respect to the one obtained using 0.088% of SPO.

Additional experiments were carried out in order to gather more detailed data about the thermal stability of the copolymers under typical processing conditions. For this reason, the polymers were heated at 300°C for 30 min in sealed glass vials, measuring the weight average molecular weight (M_w) before and after heating (Table IV).

The data reported in Table IV show that the polymers with only structure **A** are stable at the typical processing conditions of PC. On the other hand, the polymer having only structure **B** suffers of a consistent thermal degradation at 300°C. This lower thermal stability can be explained by the presence of aliphatic–aliphatic carbonate moieties that are thermally less stable compared to aliphatic–aromatic or aromatic–aromatic carbonates.[1] Therefore, we have focused the study on the thermal properties only on the polymers that did not contain structure **B**. For this reason, in order to obtain a correlation between the glass transition temperature (T_g) and aliphatic unit content, we have synthesized a series of polymers that presented only structure **A** with a molar concentration ranging from 5 to 30%. The reactions have been performed in a Brabender Plasticorder batch
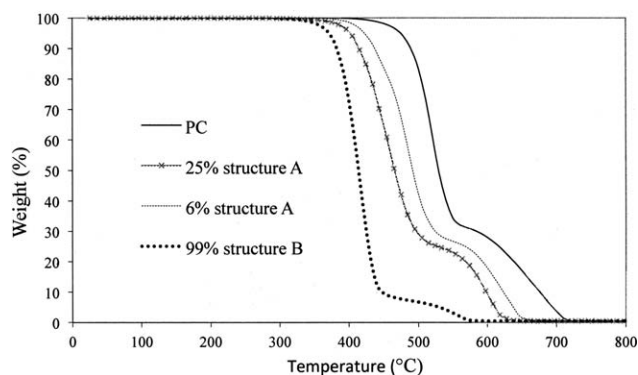
mixer, which ensures a more efficient mixing and the continuous measure of the torque, which is an indirect measure of the melt viscosity. The equilibrium torque values have been measured after 30 min when the reaction was completed. The data in Figure 6 show that the torque values decreases by increasing the ETC content. Since the copolymers prepared had molecular weights comparable with that of the starting PC (with a maximum M_w difference of 4500 with an ETC/PC molar ratio of 0.3), it is possible to conclude that the insertion of aliphatic moieties into PC backbone decreases its melt viscosity.

The glass transition temperatures (T_g) for polymers with structural unit **A** contents ranging from 5% to 30% by mol are reported in Figure 7. It is possible to observe that the T_g values follows a similar behavior compared to the torque data presented above. The DSC analyses of these polymers showed the possibility to modulate the T_g of PC in a 30°C range by the insertion of aliphatic groups. The polymer containing only structural unit **B** had a T_g of 63°C.

CONCLUSIONS

We have proved that the reaction between ETC and PC is an efficient method for inserting aliphatic groups into PC. The poly(ether-co-carbonate)s prepared by this process have a composition that depends on the ETC/PC ratio used. Using
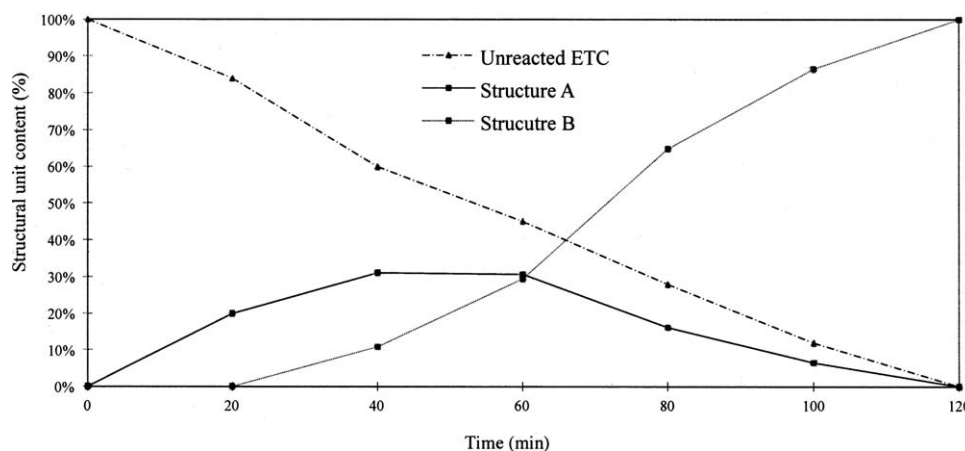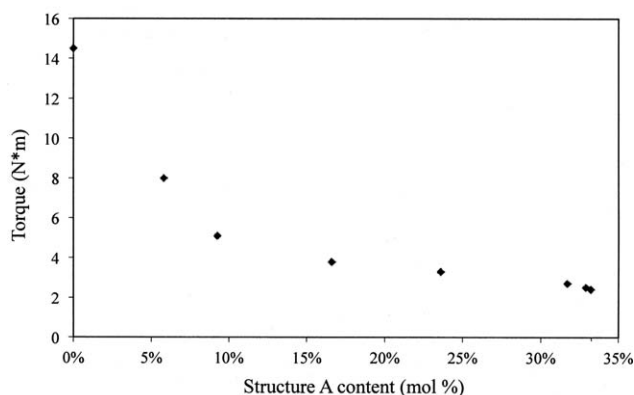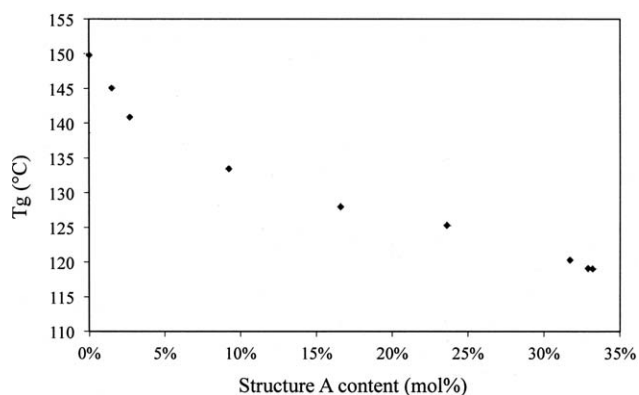

Figure 4. Structural units content during the base catalyzed reaction of ETC with PC (ETC/PC molar ratio = 2).

Table IV. Molecular Weight Before and After Heating for 30 Minutes at 300°C

ETC inserted/bisphenol moieties (%)	M_w before treatment	M_w after treatment
0	43,500	41,100
6	40,700	35,900
15	35,100	34,500
30	34,000	33,400
200	31,600	8000

Figure 7. Glass transition temperature of polymers with different structure **A** content.

ETC/PC ratios below 1, both aliphatic–aromatic carbonate and ether groups are formed. Increasing the ETC/PC molar ratio to 2 affords aliphatic–aromatic ether groups and aliphatic–aliphatic carbonate groups. The reaction mechanism has been studied in details by using model compounds and then confirmed by reactions on polymers. In the presence of a basic catalyst, the proposed mechanism involves the formation of a carbonic acid derivative that undergoes a decarboxylation reaction, leading to the formation of alkoxy anions. After reaction with aromatic carbonate groups, the latter yield aliphatic–aromatic ether linkages. Using a basic catalyst no polymer discoloration was observed and the molecular weight of the final polymers was close to that of the starting PC. The selective degradation of the polymer obtained with an ETC/PC molar ratio 2 affords the BHEEB in high yields. This compound can be used for the preparation of terephthalate polyesters with high T_g and thermal stability.

Polymers with aliphatic units content ranging from 5 to 30 mol % have been prepared in a Brabender Plasticorder mixer, showing a reduced glass transition temperature and a lower melt viscosity with respect to the starting PC. The DSC analyses of the polymers showed that the T_g of PC can be modulated in a 30°C range by the insertion of aliphatic groups. Moreover, the polymers containing aliphatic–aromatic ether moieties up to 30% by mol are stable up to 300°C, a standard processing temperature for PC.

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Figure 6. Equilibrium Torque value of Brabender Plasticorder mixer for polymers with different structure **A** contents.

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