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Chemical Modification of Bisphenol A Polycarbonate by Reactive Blending with Cyclic Anhydrides
Part 1: Reaction with Succinic Anhydride

Corrado Berti, Martino Colonna (✉)[1], Maurizio Fiorini, Cesare Lorenzetti, Laura Sisti

[1]Dipartimento di Chimica Applicata e Scienza dei Materiali
Università di Bologna, Viale Risorgimento 2, 40136 Bologna, Italy
E-mail: martino.colonna@mail.ing.unibo.it Fax: +390512093220

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Summary

Reactive blending with cyclic anhydrides in the melt is a promising process to modify the chemical structure of bisphenol A polycarbonate (PC) by insertion of ester moieties leading to consistent changes in the chemical and physical properties of PC. In particular, by the reaction with succinic anhydride it is possible to insert aliphatic moieties in the polymer backbone, decreasing the melt viscosity and the glass transition temperature of PC (and thus increase its processability). The reaction, that is catalysed by Lewis acids (e.g. titanium butoxide), proceeds through the formation of carbonyl carbonate groups that undergo decarboxylation leading to ester moieties. No side reactions have been detected by NMR analysis. The addition of phosphorous acid as catalyst quencher at the end of the process gives rise to polymers with good colour and thermal stability.

INTRODUCTION

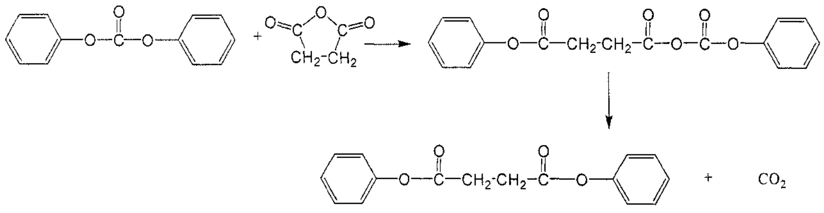
Aromatic polycarbonates, and in particular PC, constitute a widely used and versatile class of engineering thermoplastics [1-4]; for them a continued dynamic growth is expected in the next years [4,5]. The main reasons for this outstanding performance depend not only on their unique combination of useful properties and excellent price/performance balance, but also on the intrinsic capability of the polycarbonate structure to be easily and widely modified [6]. Among the most important modifications of PC, the insertion of aliphatic moieties into the PC polymer chains is used industrially [7,8] to control the glass transition temperature (Tg); a lower Tg leads to a melt viscosity reduction. Indeed, the polycarbonates possess a relatively high melt viscosity; therefore, in order to prepare a molded article from polycarbonate, relatively high extrusion and molding temperatures are required. Various efforts have been attempted throughout the years to reduce the melt viscosity of polycarbonates while retaining the desired physical properties. These methods include the use of plasticizers, the use of aliphatic chain stoppers, the reduction of molecular weight, the preparation of bisphenols having long chain aliphatic substituents and various polycarbonate copolymers as well as blends of polycarbonate with other polymers.

High molecular weight aliphatic segments have been introduced into the polycarbonate by interfacial methods using dicarboxylic endcapped polyisobutylene segments [9,10]. Great interest has been generated in successfully synthesising the poly(ester-*co*-carbonate) with aliphatic ester segments. A standard interfacial process employing the chloride derivative of the saturated aliphatic α,ω-diacids is industrially employed to prepare the poly(ester-*co*-carbonate) [7,8,11]. However, the availability of the diacid chloride starting materials is a problem because of their very high cost and low stability towards hydrolysis.

On the light of the increasing importance of the melt polymerisation process for the synthesis of PC (since it does not require the use of phosgene, which is a highly regulated hazardous chemical), we have carried out a study regarding the insertion of aliphatic and aromatic moieties into PC backbone by exchange reaction in the melt with low molecular weight compounds, in particular cyclic carbonates [12] and anhydrides. The insertion of aliphatic and aromatic groups by melt reaction can be performed during the processing of the raw polymers by reactive blending or reactive extrusion, leading to a wide range of materials with different properties starting from a single polymer.

During our work on exchange reaction on molecules containing carbonyl moieties (ester, carbonates, anhydrides, amides, etc.) we have studied the reaction between carbonate groups and anhydrides [13]. In the presence of a Lewis acid catalyst, we have observed that this reaction affords ester groups in high yields. In particular, when succinic anhydride was reacted with diphenyl carbonate at 260°C for 15 minutes, phenyl succinate was obtained in very high yields (>95% when TBT was used as catalyst, 80% when tin dibutyl dimethoxide was used). Ester moieties have also been obtained in high yields (87% when TBT is used as catalyst, 85% when tin dibutyl dimethoxide was used) by reacting hexanoic anhydride with ethylene carbonate at 260°C for 2 hours [13].

The mechanism of the reaction between carbonate and anhydride groups has also been investigated by using low molecular weight compounds (model compounds) [13]. It has been established that the reaction proceeds through the formation of an intermediate containing an ester group and a carbonyl carbonate group [14] which evolves toward the formation of the second ester group by carbon dioxide elimination.



Scheme 1: diphenyl carbonate/succinic anhydride reaction scheme.

To the best of our knowledge there are no methods in the literature for the insertion of aliphatic units in the polycarbonate backbone by reactive blending. In this paper, we report the modification of PC by melt reaction with succinic anhydride in the presence of a Lewis acid catalyst, in order to incorporate aliphatic ester moieties into the PC backbone. The thermal properties (in particular Tg and thermal stability) of the copolymers synthesised are also reported.

EXPERIMENTAL

Succinic anhydride (SA) (from Aldrich Chemicals) was crystallised from hot CH_2Cl_2 before use. Titanium(IV) tetrabutoxide (TBT) (from Aldrich Chemicals) was distilled in vacuum before use. Poly[2,2-bis(4-hydroxyphenyl)propane carbonate] (Bisphenol A polycarbonate, PC) was a gift from General Electric Plastics (M_w 52400, Tg=154°C) and was dried overnight at 130°C under reduced pressure before use.

PC/succinic anhydride reaction in glass tube: PC (2.54 g; 10.0 mmol of repeating unit), succinic anhydride (0.120 g; 1.20 mmol) and TBT (0.00320 g; 0.00930 mmol) as catalyst were placed into the glass tube (15 cm long, 2 cm internal diameter). The glass tube was then immersed into an oil bath at 260°C. Crystals of succinic anhydride were found during the reaction in the top part of the glass tube. The reaction was stopped after 30 minutes. The orange polymer was then dissolved in CH_2Cl_2, precipitated in CH_3OH and dried at 100°C under reduced pressure. The polymer was then analysed by ^{1}H-NMR (using $CDCl_3$ as solvent) and by GPC using $CHCl_3$ as eluent. The ^{1}H-NMR of this polymer is reported in the results and discussion. This reaction was repeated using succinic anhydride/PC ratio of 1 (respect to PC repeating unit) for 45 minutes; samples were taken every 5 minutes in order to measure the succinic anhydride conversion.

PC/succinic anhydride reactions in Brabender mixer: The reactions were conducted in a Brabender Plasticorder mixer series PL2000/W50. The Brabender mixer was preheated to 260°C. PC (30.0 g; 0.118 mol) was then introduced into the mixer; after 2 minutes, when all of the PC was melted, succinic anhydride (0.354 g; 3.54 mmol) was added. After the temperature was re-equilibrated at 260°C, the TBT (0.037 g, 0.110 mmol) was added. The mixer was then closed with a teflon lid and the torque was measured and recorded. The reaction was stopped after 5 minutes and the orange polymer was extracted from the Brabender. The reaction was repeated with succinic anhydride/PC molar ratio of 0.06, 0.12 and 0.30 (respect to the PC repeating unit).
In some experiments phopshorous acid (0.370 g; 4.51 mmol) was added at the end of reactive blending; in those cases the final polymer turned to transparent pale yellow after the phosphorous acid addition.
The gel permeation chromatography (GPC) measurements were performed on a HP series 1100 HPLC equipped with a Polymer Labs PL gel 5 μm mixed C column, using an UV detector set at 254 nm. CH_2Cl_2 was used as eluent. The molecular weights were determined using a calibration curve obtained from polystyrene standards.
^{1}H-NMR spectra were recorded with a Varian XL-300 spectrometer (chemical shifts are downfield from tetramethylsilane (TMS)).
Differential scanning calorimetry (DSC) analysis was performed using a Perkin Elmer DSC7. The instrument was calibrated with high purity standards (indium and phenanthrene). Dry nitrogen was used as purge gas. The samples (ca. 5 mg) were

heated from room temperature to 200°C at 20°C/minute (1^{st} scan) and then rapidly quenched to room temperature. The sample was then reheated to 200°C at 20°C per minute (2^{nd} scan). The T_gs were measured on the second scan in order to erase the previous thermal history and provide the same heat treatment to all the samples. The T_g was taken as the midpoint of the heat capacity increment ΔC_p associated with the glass transition.

The thermogravimetric curves were recorded in air using a Perkin Elmer TGA7 apparatus (gas flow: 50mL/min) with a 10°C/min heating rate from 25°C to 900°C.

RESULTS AND DISCUSSION

On the basis of the high yield and short reaction times in the presence of TBT as catalyst observed using low molecular weight compounds [13], we have applied the reaction between carbonates and anhydrides for the incorporation of aliphatic units into PC polymer chain. The reactions have been conducted in a glass tube at 260°C in order to have short reaction times (according to model reactions) and minimise the thermal degradation of the final polymer. The ^{1}H-NMR spectrum of the polymer synthesised by reacting PC with 12% succinic anhydride at 260°C, in the presence of TBT as catalyst is reported in figure 1. The doublet at 6.95 ppm can be assigned to aromatic protons of bisphenol A units linked to aliphatic ester moieties. The peak at 2.95 ppm can be ascribed to the methylene groups of the reacted anhydride, while the unreacted anhydride gives rise to a singlet at 2.99 ppm. No unreacted anhydride was found after 30 minutes at 260°C when 12% of SA was used. For longer reaction times or higher catalyst levels a doublet at δ=6.70 due to phenolic end groups, deriving from degradation reactions, has been observed. The ^{1}H-NMR analysis did not show the formation of any other structural unit by side-reactions.

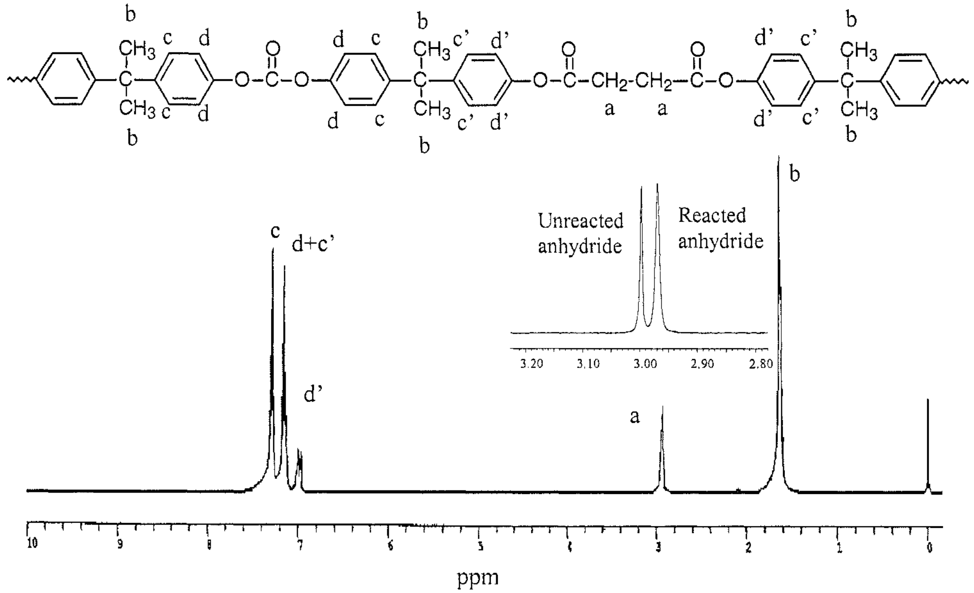
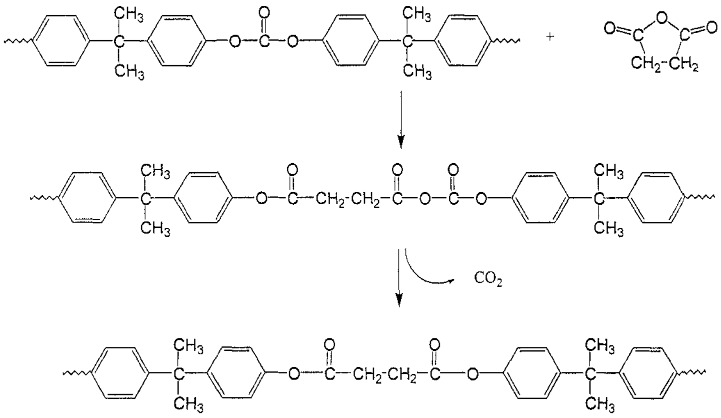


Figure 1: ^{1}H-NMR spectrum of PC after reactive blending with succinic anhydride. The insert is an expanded portion of the spectrum of a sample taken at 50% succinic anhydride conversion.

On the basis of the results obtained with model compound reactions and of the NMR analysis of the reacted PC, the scheme 2 can be proposed for the reaction between PC and cyclic anhydrides. The ethylene insertion by exchange reaction gives rise to the formation of an intermediate containing a carbonyl carbonate group (though again in this case no direct evidence for the formation of the intermediate was found) and an ester group. The carbonyl carbonate group decomposes at the reaction temperature leading to the formation of the second ester group and CO_2.



Scheme 2: SA/PC reaction scheme.

The reaction was then performed using a SA/PC molar ratio of 1, taking samples of the reaction melt in order to determine the anhydride conversion and the molecular weight change (table 1).

Table 1: SA conversion versus time in SA/PC reactive blending at $SA/PC_{RU} = 1$ (PC_{RU} = PC repeating units).

Reaction time (min)	$\frac{SA_{inserted}}{SA_{inserted} + SA_{unreacted}} \cdot 100$	M_W (GPC)
0	0	52400
10	0	46500
20	15	42900
25	55	39600
35	94	36500
45	100	34500

The extent of the reaction was evaluated by ^1H-NMR comparing the doublet at 6.95 ppm corresponding to the two aromatic protons close to the ester moieties with the total aromatic protons signals. The anhydride conversion was evaluated by comparison of the singlet at 2.99 ppm corresponding to the unreacted anhydride with the singlet at 2.95 ppm corresponding to the ester methylene group. No unreacted anhydride was present after 45 minutes, however, only 34% of the anhydride was incorporated in the polymer backbone since 66% of the starting anhydride was lost due to evaporation when the reactor was opened to take the samples. A molecular weight drop due to degradation reactions was also observed.

In order to assess the contribution of thermal degradation and of the reaction with the catalyst to the molecular weight decrease, PC was reacted with TBT with or without SA in molar ratio equal to one, under the same conditions used for the reactive blending. Samples taken every 5 minutes were analysed by GPC to measure Mw. The Mw data as a function of reaction time, reported in figure 2, show that the titanium catalyst is the main cause for the degradation reactions and that the degradation proceeds during the reaction. For this reason low catalyst levels and short reaction times are needed to obtain high molecular weight polymers.

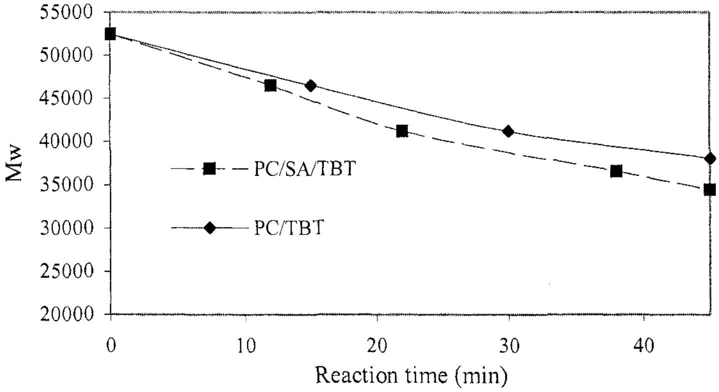


Figure 2. Molecular weight change during reactive blending.

The thermal stability of the polymer samples modified by SA was studied by thermogravimetric analysis. It is indeed well known that titanium derivatives decrease the PC thermal stability and produce a consistent discoloration. For this reason phosphorous acid was added as catalyst quencher at the end of the reaction to improve thermal stability and reduce polymer discoloration [15,16]. The positive effect of phosphorous acid as catalyst quencher can be observed in figure 3, since a lower decrease in thermal stability respect to starting PC can be observed for the modified polymer after the addition of phosphoric acid. Moreover, the weight loss starts at temperatures exceeding 350°C that is well above than the usual PC processing temperature. The final polymers turned from light brown to transparent pale yellow after quencher addition.

The reaction was also conducted in a Brabender Plasticorder in order to have a more efficient mixing and an indirect measure of the melt viscosity by means of the torque gauge signal. The results obtained are reported in table 2. Copolymers with higher molecular weight have been obtained using the Brabender mixer due to the shorter reaction times required for the complete anhydride insertion.

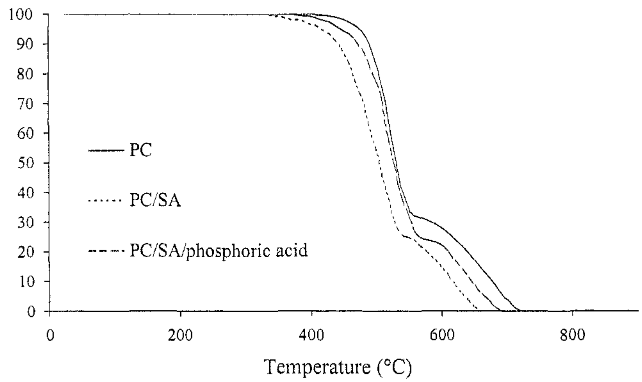


Figure 3. TGA analysis results.

Table 2. Reactive blending of SA/PC in Brabender at different SA/PC $_{RU}$ molar ratios.

$\frac{SA_{fed}}{PC_{RU}}\cdot 100$	Reaction time (min)	$\frac{SA_{inserted}}{PC_{RU}}\cdot 100$	M_W (GPC)
0	5	-	47300
3.0	5	2.4	46800
6.0	10	5.8	44100
12.0	15	11.1	45700
30.0	20	25.6	45100

The NMR analysis showed that at the end of the reactions no unreacted SA was present in the polymer melts, although the amount of ester moieties in the polymers was always lower compared to the amount of anhydride added at the beginning of the reactions. 10-20% of SA fed to the mixer was lost due to evaporation. The polymer containing 100% ester moieties, i.e. the poly(bisphenol A succinate), was also prepared, but it was necessary to use a 1.4 fold excess of succinic anhydride and a longer reaction time (60 minutes). In this case, the molecular weight of the final polymer was fairly low (Mw=25400).

As reported in figure 4, the torque signal of the Brabender at the end of the reaction, decreased with the increase in SA content indicating that, since the polymers obtained had comparable molecular weights, the insertion of aliphatic moieties in the PC chain improves its mobility. Indeed, the results in figure 5 show that it is possible to modulate the glass transition temperature in a 20°C range by the insertion of succinic anhydride. This results are very important since our main goal was to decrease PC melt viscosity and therefore to improve the processability of the material.

CONCLUSIONS

Reactive blending with succinic anhydride is a promising process for the modification of the chemical structure of PC by insertion of aliphatic ester moieties in the polymer backbone leading to consistent changes in the chemical and physical properties of PC. The melt viscosity and the glass transition temperature of modified PC can be reduced thus increasing its processability. The reaction, that is catalysed by Lewis acids (e.g. titanium butoxide), proceeds trough the formation a carbonyl carbonate groups that after decarboxylation leads to ester moieties. No significant side reactions have been detected by ^{1}H-NMR analysis apart from the degradation due to the catalyst. The addition of phosphorous acid as catalyst quencher at the end of the reaction gives rise to polymers with good colour and thermal stability. The Mw decrease and the insertion of soft blocks should give both rise to a decrease in modulus and therefore this modified PC could be preferably used in application were high melt flow is required and no stringent requirements for mechanical properties are needed (e.g. lamp covers and complicated thin walls parts).

Further studies on aromatic anhydrides and aliphatic polyanhydrides are in progress and will be reported in a following paper.

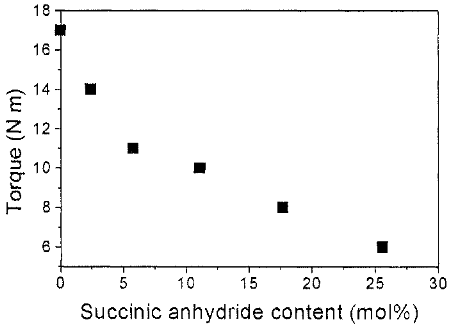


Figure 4. Torque final signal as a function of SA inserted in PC backbone.

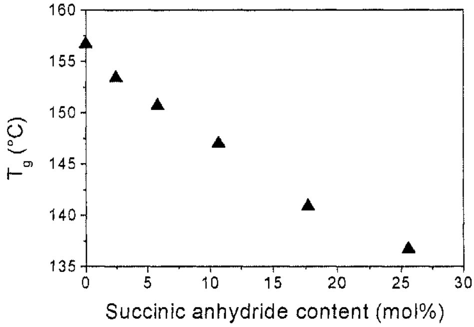


Figure 5. Glass transition temperature as a function of SA inserted in PC backbone.

REFERENCES

1. Christopher WF, Fox DW (1962) Polycarbonates. Reinhold Publishing, New York
2. Schnell H (1964) Chemistry and Physics of Polycarbonates, Polymer Reviews. Interscience Publishers, New York, Vol 9
3. Serini V (1987) Ulmann's Encyclopedia of Industrial Chemistry. Kaudy L, Rounsaville JF, Schulz G (eds) VCH Weinheim, Vol A21, p 207
4. Bostick, EE (2000) In: Legrand, DG; Bendler JT (eds) Handbook of Polycarbonate Science and Technology. Marcel Dekker, New York pp1-6
5. Thayer A (1998) Chem Eng News 76:20
6. Freitag D, Fengler G, Morbitzer L (1991) Angew Chem 30:1598
7. Fontana LP, Buckley PW (1991) US Pat 5,025,081
8. Fontana LP, Reed RA (1985) US Pat 5,455,323
9. Mark V, Peters N (1987) US Pat 4,677,183
10. Mark V, Peters N (1986) US Pat 4,628,081
11. Kochanowski JE (1981) US Pat 4,286,083
12. Berti C, Colonna M, Fiorini M, Marianucci E, Sisti L. Submitted to Macromolecules
13. Berti C, Colonna M, Sweileh B, Marianucci E, Pilati F (1999) Synth Comm 29 (6): 917
14. Tarbell DS, Leister NA (1958) J Org Chem 23:1149
15. Kawase S, Shima T, Inata H, Kurisu S (1974) DE 2414849
16. Kuze S, Suga K (1996) JP 08143658