

# Catalytic Transesterification in Polycarbonate–Polycaprolactone Systems

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## SYNOPSIS

Bisphenol A polycarbonate (PC)–poly- $\epsilon$ -caprolactone (PCL) blends have been prepared by melt mixing in the presence of different catalysts using a Brabender plastograph and single-screw extruder at 240–260°C. Increased crystallizability [detected by differential scanning calorimetry (DSC)] of the PC component was observed in the blends obtained in the presence of *p*-toluenesulfonic acid. Acceleration of carbonate–carbonate exchange reactions is suggested as the main reason for the crystallizability enhancement. Results of solubility tests, DSC, and infrared (IR) spectroscopy evidence ester–carbonate transesterification taking place during PC–PCL blending in the presence of tetrabutoxy titanium and dibutyltin dilaurate. © 1994 John Wiley & Sons, Inc.

## INTRODUCTION

Exchange reactions occurring during melt mixing of polycondensation thermoplastics are of interest, because reaction products of commercial potential may be obtained. The reactions, taking place during blending of bisphenol A polycarbonate (PC) and different polyesters, have been a subject of several papers.<sup>1–16</sup>

In an early study of PC–poly(*butylene terephthalate*) (PBT) miscibility characteristics, a suggestion was made that the observed minor variation of the  $T_g$ 's with blend composition and the PBT melting point depression may be a result of interchange reactions occurring during the high-temperature melt processing.<sup>1</sup> Later, the transesterification reaction hypothesis, proceeding in the PC–PBT system, was proved.<sup>2–5</sup> The mechanism and kinetics of the exchange reactions and the structure of the reaction products were studied using infrared (IR), nuclear magnetic resonance (NMR), and solubility tests.<sup>3–5</sup> The most likely mechanism of the PC–PBT reaction is a direct ester–carbonate interchange yielding copolyesters. Resulting structures of the

reaction products depend on the reaction time. At short reaction times, block copolyesters with low solubility in CH<sub>2</sub>Cl<sub>2</sub> are formed. As the reaction time increases, the blocks become shorter, the composition of the copolyesters becomes more random, and the solubility increases. The reaction was found to be catalyzed by some organotitanates (which, in turn, may be deactivated by some organic phosphites) and strongly promoted by temperature. Gas evolution observed during the melt-mixing step was considered to be a result of a side reaction described as acidolysis of PC by carboxyl end groups.

The first conclusion concerned with transesterification reactions occurring in a PC–poly(*ethylene terephthalate*) (PET) system was that very few, if any, interchange reactions take place between the ester and carbonate groups during melt mixing.<sup>6</sup> However, further investigations have shown that PC does react with PET, but much slower than with PBT, and that the presence of a transesterification catalyst is needed to make the reaction significant.<sup>7–9</sup> Selective degradation of PC sequences, solubility tests, and IR and NMR spectroscopy were used to study the reaction course and their products. A direct ester–carbonate interchange, similar to that in the PC–PBT system, was assumed to be the main reaction occurring in molten PC–PET mixtures.<sup>7,8</sup> The chemical structure of the final reacted blend appears

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to be strongly dependent both on the melt-mixing time and on the type of interchange catalyst. For long times of mixing intramolecular exchange reactions, leading to the formation of cyclic ethylene carbonate (EC), and a decarboxylation reaction, leading to the formation of aromatic-aliphatic ether moieties, have to be taken into account. Elimination from the reaction medium of EC, which is sufficiently volatile and unstable, may shift the equilibrium toward the formation of a polymer richer in aromatic groups.<sup>8</sup> The reactions are activated to some extent by antimony compounds (residual catalyst from the PET synthesis) and are strongly accelerated by the addition of tetrabutoxy titanium,  $\text{Ti}(\text{OBU})_4$ . Discoloration (from white to yellow) due to the formation of titanium-containing byproducts and gas evolution due to acidolysis of carbonate groups by end carboxyls followed by decarboxylation were observed as the transesterification reaction in the presence of titanium catalyst proceeded.

Binary systems of PC with copoly[cyclohexanedimethanol (iso/tere)phthalate] (PcHITP), the latter a semicrystalline copolyester based on 1,4-cyclohexanedimethanol and a mixture of terephthalic and isophthalic acids, were initially studied using differential thermal analysis (DTA) and dynamic mechanical analysis (DMA). The two polymers were found to be completely miscible in the amorphous phase. The role of ester-carbonate interchange reactions in these studies was deemed unimportant.<sup>10</sup> However, a subsequent in-depth investigation has shown that PcHITP crystallizability in 50 : 50 PC-PcHITP blends decreases significantly as the residence time of the melt at 277°C increases, while that of the 100% PcHITP remains practically unchanged for at least 20 min. The decline of PcHITP crystallizability, as indicated by measuring melting endotherm magnitudes of blends annealed at 177°C, is accelerated by the presence of  $\text{Ti}(\text{OBU})_4$  and is retarded in the presence of some arsenic and phosphorous compounds.<sup>11</sup> It was thus concluded that ester-carbonate interchange reactions did occur in the molten state of the blends. These reactions are catalyzed by the residual titanium catalyst from the PcHITP formation step. As reactions proceed, the blend gradually converts into a copolymer, resulting in a reduction of the PcHITP component crystallizability and an increase in solubility of the blend in  $\text{CHCl}_3$ . Blends discoloration, accompanying the melt processing, was shown to be due to interaction between the titanium compound and the phenolic end groups of the PC component. Arsenic oxides and phosphorous stabilizers deactivate the titanium catalyst, thus effectively suppressing both the trans reactions and color formation.

*Poly(bisphenol-A terephthaloyl-isophthaloyl copolyester)* (PAr) was shown to react with PC even without any catalyst added if thermally treated at 250°C.<sup>12,13</sup> The block copolymer formation and its subsequent conversion into random copolymers were traced by differential scanning calorimetry (DSC), NMR, and gel permeation chromatography (GPC).

Cruz et al.<sup>14</sup> studied uncatalyzed melt mixed PC-polycaprolactone (PCL) system using DTA and DMA techniques. They observed a single  $T_g$ , which was attributed to physical miscibility, and some melting point depression for PCL. In these uncatalyzed blends no evidence of transesterification or copolymer formation during melt mixing (260°C) were revealed. In another report by Fernandes et al.<sup>15</sup> an MPC (tetramethyl bisphenol A polycarbonate) and PCL system was studied. The PCL melting point depression was used to calculate interaction energy density via the Nishi-Wang plot. The calculated negative value for interaction energy density was thought to be proof of some thermodynamic interaction. Later, Jonza et al.,<sup>16</sup> using the Hoffman-Weeks plot, calculated the PCL equilibrium melting point of PCL when present in the PC-PCL blend, which was found to be equal to that of the pure PCL. Therefore, they claimed that the observed melting temperature depression is due to some changes in crystal morphology rather than to thermodynamic interactions. Fourier transform infrared (FTIR), NMR, solubility tests, and turbidimetric titration were also employed in this work to study the reactivity of a 50 : 50 PC-PCL uncatalyzed blend.<sup>16</sup> The blend was prepared by codissolution in  $\text{CH}_2\text{Cl}_2$  with subsequent flush casting onto preheated dishes and annealing for various periods at 250°C in a vacuum oven (without melt mixing). They found that PCL solubility in  $\text{CCl}_4$  dropped rapidly during the first 15 min of thermal treatment and then leveled off at 10% extractability. Prolonged exposure of the blend to 250°C produced a gelled sample that swelled only in  $\text{CH}_2\text{Cl}_2$ , suggesting chemical reactions to take place. Proton NMR spectra of the  $\text{CCl}_4$  extract of the reaction mixture has shown evidence of  $-\text{CH}$  group presence in addition to the  $-\text{CH}_3$  and  $-\text{CH}_2$  groups, indicating the existence of branch points in the chain. Based on the solubility results and lack of evidence of transesterification, the reactions were attributed to the thermo-oxidative branching mechanism and not to ester-carbonate exchange. The FTIR method was found to lack sufficient sensitivity for this pair of polymers, since the expected band frequencies of new groups are too close to those of the existing ones.<sup>16</sup>

In summary, the foregoing literature review has shown that carbonate-ester reactions lead to co-

polymer formation during melt mixing of PC with some polyesters. IR, NMR, DSC, and solubility tests were used to prove the reaction occurrence and progress. Catalyst addition is needed in some cases to promote these reactions, which otherwise may be undetectable. Titanium compounds were found to be effective catalysts for transesterification.

The only systems, among the reviewed ones, where the carbonate-ester exchange reaction was not revealed are the PC-PCL uncatalyzed blends. In the present work an attempt was made to find suitable conditions to cause transesterification in PC-PCL catalyzed blends.

## EXPERIMENTAL

### Materials

Commercial PC (Lexan 103, GE) and commercial PCL (PCL 700, Union Carbide) were used. The polymers were separately vacuum dried, to prevent hydrolysis, prior to melt processing.

The main interchange reactions expected to take place in a PC-PCL system are acidolysis between carboxyl end groups of PCL with carbonate groups and transesterification between ester and carbonate groups. The first stage of both reactions is the same: a heterolysis of the  $\text{—CO—O—}$  bond. Depending on the type of catalyst present, acidolysis, esterolysis, or direct transesterification may be catalyzed. In the present study the following substances were used as potential catalysts of trans reactions:

*Catalysts of acidolysis:* *p*-toluenesulfonic acid (*p*-TSA)<sup>17,18</sup> and adipic acid (AA)<sup>17</sup>

*Catalyst of esterolysis:* dimethyl terephthalate (DMTPH)<sup>17</sup>

*Catalysts of direct transesterification:* *i*-PrO-Ti(OEt-NH-Et-NH<sub>2</sub>)<sub>3</sub> (KR-44),<sup>17</sup> tetrabutoxy titanium [Ti(OBu)<sub>4</sub>],<sup>5,13,17</sup> dibutyltin dilaurate (DBTDL),<sup>17</sup> and triphenyl phosphite (TPP).<sup>19</sup> All catalysts were reagent grade and were used as supplied.

### Reactive Melt Mixing of PC-PCL Blends

Reactive mixing of PC with PCL was carried out either in a Brabender plastograph or in a single-screw extruder. Two typical procedures of melt processing are reported below.

#### Brabender Plastograph

Weighed dry pellets of PC and PCL were fed into the mixing head of a Brabender plastograph (blade speed 50 rpm) preheated to 240°C. This processing temperature was selected to prevent PC crystallization and also to minimize thermo-oxidative reactions. A catalyst was added 10 min after torque stabilization, and the mixture was then allowed to react for 15 min. The total residence time in the molten state, including the charging step, did not exceed 35 min. Noticeable distinctions from the behavior of the respective physical blends, such as sharp torque changes, discoloration, and gas evolution after catalyst addition, served as preliminary indications of chemical reactions taking place (Table I). No visible effects were observed upon AA, DMTPH, or TPP addition to the molten blends undergoing mixing. It was thus assumed that these substances are not sufficiently effective to promote ester-carbonate exchange reactions. The introduction of *p*-TSA, Ti(OBu)<sub>4</sub>, KR-44, and DBTDL resulted in a noticeable torque reduction, and the titanium compounds also caused discoloration and gas evolution.

#### Single-Screw Extruder

In a separate series of experiments, PC-PCL, PC-PCL-TPP, and PC-PCL-DBTDL blends (containing 25% PCL) were prepared by extrusion. Titanium catalysts were not used because of their strong activity in accelerating side reactions and a tendency to colored complex formation.<sup>11</sup> Pellets of the two polymers were dry blended and then mixed with catalyst, which was added dropwise. The mixtures were subsequently processed in a single-screw

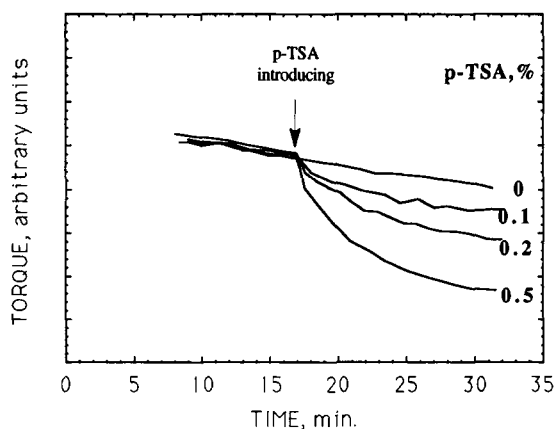
**Table I** Visual Observations during Melt Mixing of PC-PCL 75 : 25 Blends

Catalyst	Content (%)	Torque Changes	Discoloration	Gas Evolution
<i>p</i> -TSA	0.1-1	+	+	-
AA	1	-	-	-
DMTPH	1	-	-	-
Ti(OBu) <sub>4</sub>	0.1-1	+	+	+
KR-44	0.2-0.4	-	+	+
DBTDL	0.1-1.6	+	-	+
TPP	1-2	-	-	-

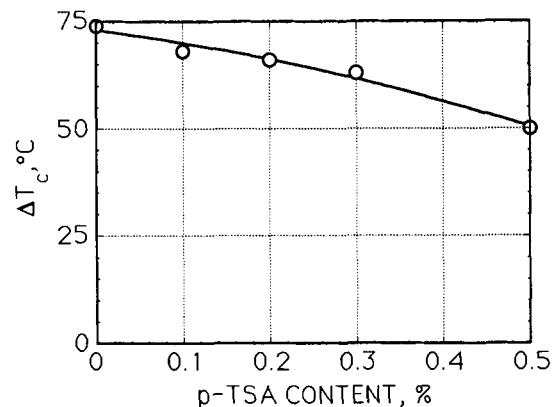
extruder at 250°C (constant temperature was maintained along the cylinder and die). The molten blends appeared milky white upon exiting the die but became more and more clear while cooling, indicating the phenomenon of a lower critical solution temperature previously reported for this system.<sup>14</sup> Some blends, believed to undergo transesterification, were further tested to detect copolymer formation.

### Characterization Techniques

Melt flow index (MFI) was measured using a Davenport melt indexer with a standard 2.1-mm die at 250°C, 2.16-kg load. Rheological properties were studied using a capillary Instron rheometer at 235°C,  $D = 1.27$  mm,  $L/D = 40$ . DSC analysis was carried out using a Mettler TA3000 system under N<sub>2</sub> atmosphere. Samples were heated for 10 min at 250°C in the DSC instrument and then slowly cooled (10°C/min) before testing unless otherwise indicated. Carbon tetrachloride, a good solvent for PCL and nonsolvent for PC, was used in Soxhlet extraction of the blends to determine the content of non-reacted extractable PCL. Gel formation was determined by dissolving the blends in CHCl<sub>3</sub>, a common solvent for PC and PCL. IR spectra were recorded using Perkin-Elmer IR and Mattson FTIR instruments. Two to 3% CHCl<sub>3</sub> solutions were tested. Solutions rather than solid samples were chosen to avoid complications concerning changes in the CO stretching band frequency, depending on the physical (amorphous or crystalline) state of PC and PCL.<sup>20</sup> As the PC was the major component of the studied blends and was removed to only a small extent during CCl<sub>4</sub> extraction, the PC carbonyl band at 1770 cm<sup>-1</sup> was used as internal reference in estimating the blends composition.<sup>20</sup>



**Figure 1** Effect of *p*-TSA content on the torque changes during melt mixing of 80 : 20 PC-PCL blends.



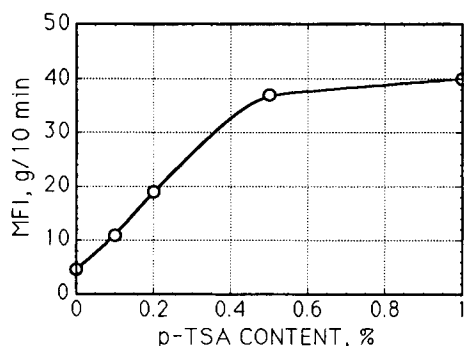
**Figure 2** Supercooling level of the 80 : 20 PC-PCL blends (cooling rate 10°C/min) as affected by *p*-TSA content.

## RESULTS AND DISCUSSION

### Acidic Catalyst

The blends containing *p*-TSA were darker than their respective physical blends. A noticeable torque reduction was observed less than a minute after catalyst addition. The magnitude of torque reduction gradually increased with the amount of catalyst added (Fig. 1), indicating reduction of the melt viscosity. The effect of *p*-TSA on 80 : 20 PC-PCL blend crystallizability is shown in Figure 2. The crystallizability of a given polymer may be characterized by the level of supercooling,  $\Delta T_c = T_m - T_c$ , where  $T_m$  and  $T_c$  are the melting on heating and crystallization on cooling temperatures, respectively. In the 80 : 20 PC-PCL blends  $\Delta T_c$  decreases as the *p*-TSA content increases, thus manifesting PC crystallizability enhancement. PC-PCL blends containing 10% PCL follow the same behavior pattern upon *p*-TSA addition. The MFI of the 90 : 10 blends increases with *p*-TSA concentration (Fig. 3), i.e., the melt viscosity decreases. While the 90 : 10 PC-PCL physical blend is amorphous, blends containing *p*-TSA exhibit PC crystallization exotherms at about 170°C (followed by a PC melting endotherm at about 220°C), and its magnitude increases with *p*-TSA content (Fig. 4); thus, the PC crystallizability increases.

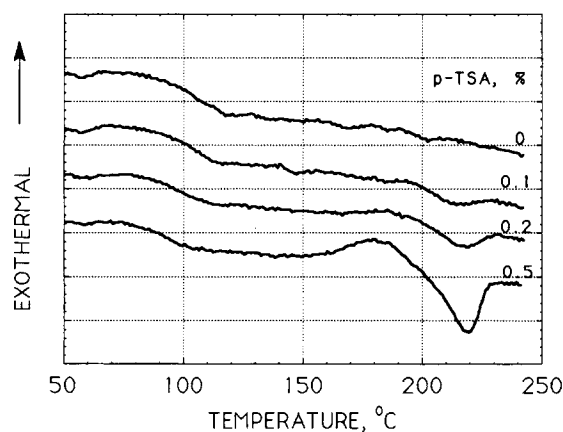
Transesterification reactions initially lead to block-copolymer formation and to a decreasing regularity of the chemical structure and order of submolecular organization. Thus, a reduction of crystallizability and crystallinity of the blend components is expected.<sup>11</sup> However, the increased crystallizability observed in the *p*-TSA-PC-PCL



**Figure 3** Effect of *p*-TSA content on the melt flow index of the 90 : 10 PC-PCL blends.

system is thus strong evidence against the occurrence of ester-carbonate trans reactions. Moreover, based on the viscosity reduction and DSC results, *p*-TSA may be suggested to catalyze carbonate-carbonate rather than ester-carbonate exchange reactions in the 90 : 10 and 80 : 20 PC-PCL blends. In such blends of polycondensation polymers (polyesters, polyamides, polycarbonates), reactions of chain transfer with chain rupture have been reported to cause molecular weight modification toward the most likely equilibrium molecular weight distribution.<sup>21</sup> This process of chain scission in the presence of *p*-TSA is a gradual one, forming a more uniform molecular weight distribution. Consequently, the gradual elimination of the longer chains explains both the decreasing blend viscosity and the increasing PC crystallizability.

Control experiments of a PC-*p*-TSA 100 : 0.5 system, being melt processed under similar conditions, was found to behave like the above-described PC-PCL-*p*-TSA blends in exhibiting discoloration



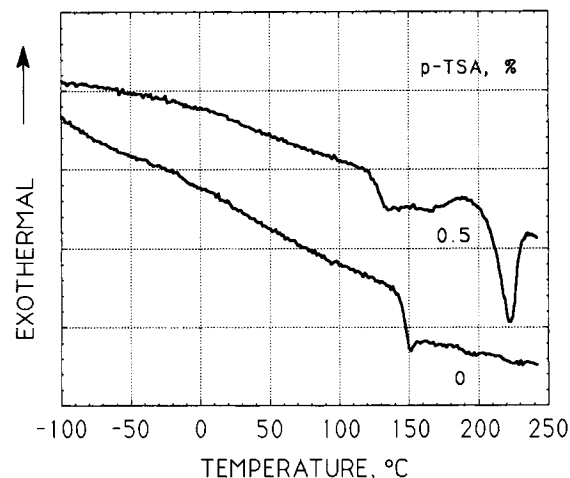
**Figure 4** Effect of *p*-TSA content on the thermograms of the 90 : 10 PC-PCL blends (first run).

and torque reduction upon *p*-TSA addition. The MFIs of PC and PC-*p*-TSA 100 : 0.5 were 2 and 14.6 g/10 min, respectively. A PC melting endotherm was observed in the DSC trace of the PC-*p*-TSA, being absent, as usual, in the untreated PC (Fig. 5). The control experiments thus confirm that the phenomena observed in the melt processing of the PC-PCL blends in the presence of *p*-TSA are explained by PC-PC rather than PC-PCL interchange reactions.

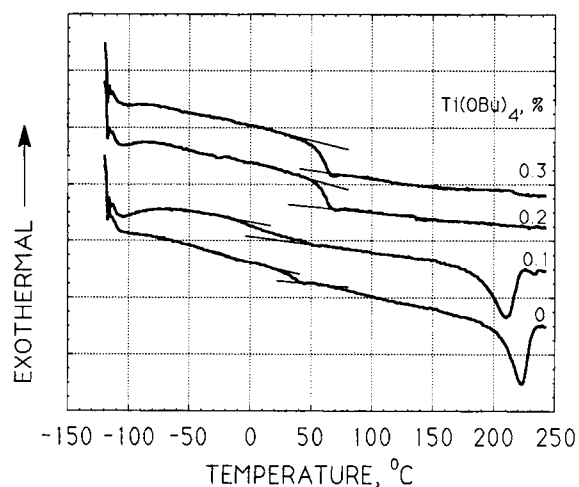
### Titanium Compounds

Both KR-44 and  $\text{Ti}(\text{OBU})_4$  have caused torque reduction upon their addition to 90 : 10, 85 : 15, 75 : 25, and 70 : 30 PC-PCL blends during melt mixing in a Brabender mixing head. Significant discoloration of the blends (from white to orange red) took place upon the catalyst's introduction. The titanium compounds have also caused gas evolution, as was evidenced by foaming of the molten blends. Qualitatively, the observed phenomena were similar upon the addition of KR-44 or  $\text{Ti}(\text{OBU})_4$ , but they were more pronounced in the latter case. Thus, further studies of the effect of titanium compounds were carried out using only  $\text{Ti}(\text{OBU})_4$ .

DSC studies reveal that  $\text{Ti}(\text{OBU})_4$  affects differently the PC-PCL blends, as compared to the *p*-TSA catalyst action. A clear PC melting peak at about 220°C and a glass transition at about 30°C are seen in the DSC trace of the uncatalyzed (physical) 75 : 25 PC-PCL blend (Fig. 6). The PCL presence at this level sufficiently plasticizes PC to promote its crystallization, an effect found also in the presence of some PC solvents. At 0.1%  $\text{Ti}(\text{OBU})_4$  a



**Figure 5** Effect of *p*-TSA on neat PC thermal behavior.



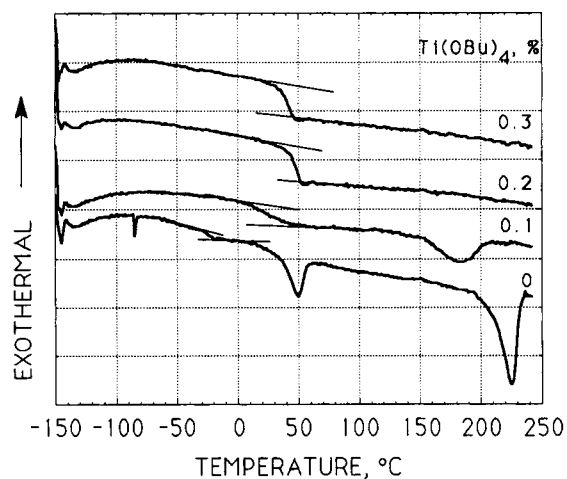
**Figure 6** Effect of  $\text{Ti}(\text{OBu})_4$  content on the thermograms of the 75 : 25 PC-PCL blends.

reduction of the PC melting endotherm is observed along with its broadening and shifting to a lower temperature. Additionally, the glass transition becomes broader. At the higher  $\text{Ti}(\text{OBu})_4$  catalyst contents the melting endotherm disappears and the glass transition shifts toward higher temperatures ( $50\text{--}60^\circ\text{C}$ ) and becomes sharp and distinct. Visually, the 75 : 25 PC-PCL blends containing 0.2 and 0.3%  $\text{Ti}(\text{OBu})_4$  are transparent (being orange red in color), while the untreated physical blend is opaque due to its crystallinity. Thus, in contrast to the *p*-TSA catalyst action,  $\text{Ti}(\text{OBu})_4$  causes the PC crystallizability to decrease. The PCL crystallizability in 70 : 30 PC-PCL blends decreases too (Fig. 7). A DSC thermogram of the physical uncatalyzed blend clearly shows endothermic melting peaks of both PCL and PC at  $50$  and  $225^\circ\text{C}$ , respectively, proving the coexistence of two crystalline phases. (At 30% PCL is beyond its saturation miscibility in PC, ca. 25%.) As the titanium catalyst content increases, initially a broad transition region appears instead of the PCL sharp melting peak along with reduction and disappearance of the PC melting peak. As the  $\text{Ti}(\text{OBu})_4$  content reaches 0.3%, a single sharp glass transition region is observed in the thermograms without any melting endotherm presence. The glass transition region first broadens, then becomes sharp and distinct, and then further increases and shifts toward higher temperatures (a similar behavior was depicted in Fig. 6 for the 75 : 25 PC-PCL blends).

The reduction of crystallinity observed in the  $\text{Ti}(\text{OBu})_4$ -catalyzed PC-PCL blends and the glass transition changes serve as arguments in favor of copolymer formation. Small amounts of catalyst

(0.1%) result in block-copolymer formation, characterized by a reduced degree of crystallinity and highly heterogeneous amorphous regions (broad glass transition). As the catalyst content increases, internal chain randomization increases, crystallization is eliminated, and a more uniform amorphous phase is produced. Solubility tests and IR spectra further support the reality of ester-carbonate exchange reactions in the PC-PCL- $\text{Ti}(\text{OBu})_4$  systems.

The 70 : 30 PC-PCL physical blend and the 70 : 30 : 0.1 PC-PCL- $\text{Ti}(\text{OBu})_4$ -reacted blend were treated with  $\text{CCl}_4$  for 48 h in a Soxhlet extractor. The soluble weight fraction was about 24% for the physical blend, while that of the reacted blend was only 13%. IR spectra of the soluble fraction showed, in the  $1700\text{--}1800\text{-cm}^{-1}$  range, a strong  $\text{C}=\text{O}$  stretching band of aliphatic ester groups with its maximum at  $1730\text{ cm}^{-1}$  and a band of low intensity at  $1770\text{ cm}^{-1}$ , associated with fully aromatic carbonate groups. Thus, the soluble fraction is mainly PCL, soluble in  $\text{CCl}_4$ , with some PCL-rich PCL-PC block copolymer, and/or PC of reduced chain length. The increased PCL component which has remained in the insoluble fraction could be due to catalyzed interchange reactions (in addition to thermally induced ones) between PCL and PC, resulting in the formation of PC-rich block-copolymer chains, insoluble in  $\text{CCl}_4$ . Besides, crosslinking of PCL or PC could also decrease the PCL solubility due to either insoluble PCL gel formation or partial trapping of PCL macromolecules in a PC gel. To test the hypothesis of gel formation, PCL and PC were separately melt treated with  $\text{Ti}(\text{OBu})_4$ . Each



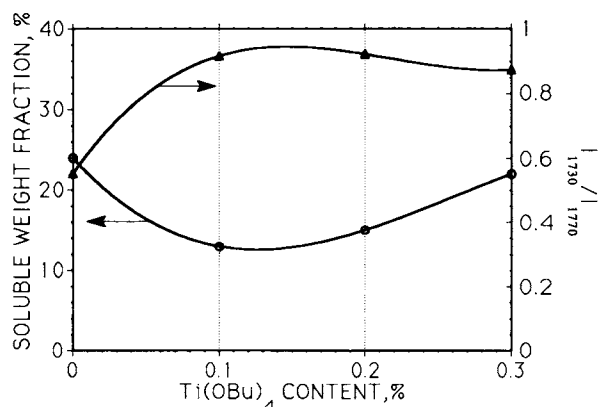
**Figure 7** Effect of  $\text{Ti}(\text{OBu})_4$  content on the thermograms of the 70 : 30 PC-PCL blends.

reaction product was found to be soluble in chloroform, thus ruling out this hypothesis.

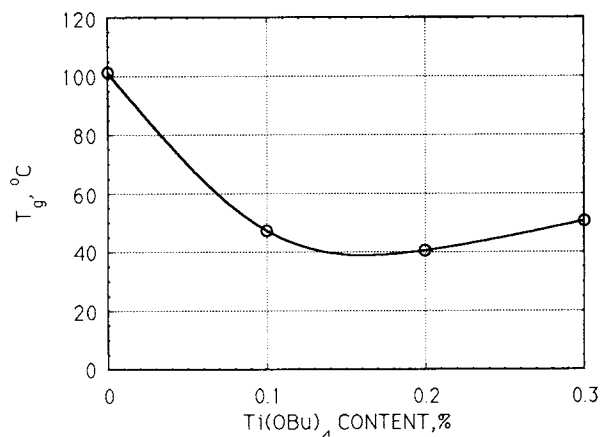
The  $\text{CCl}_4$  insoluble residue of the PC-PCL 70 : 30 physical uncatalyzed blend has shown a low peak at  $1730\text{ cm}^{-1}$ , proving that PCL is almost but not completely removable from the blend. On the contrary, the IR spectra of the insoluble residue of the PC-PCL-Ti(OBu)<sub>4</sub> 70 : 30 : 0.1 reactive blend exhibits a much more pronounced  $1730\text{-cm}^{-1}$  absorption peak, indicating the presence of a significantly higher PCL content. The composition of the insoluble PC-PCL 70 : 30 fractions and their quantity depend on the titanium catalyst concentration, as shown in Figure 8. The maximum PCL content in the insoluble residue, determined by the relative intensity of the  $1730\text{-cm}^{-1}$  IR peak, occurs at 0.15% Ti(OBu)<sub>4</sub>, a concentration corresponding also to the minimum blend solubility (maximum insoluble fraction).

DSC data are in accordance with the IR and solubility test results. The  $T_g$  of the PC-PCL blends decreases as PCL, acting as a polymeric plasticizer, content increases. The  $\text{CCl}_4$  insoluble fraction of the physical blend [0% Ti(OBu)<sub>4</sub>] exhibits a  $T_g$  of  $100^\circ\text{C}$ , indicating that this fraction includes some PCL ( $T_g$  of PC is  $150^\circ\text{C}$ ), as also observed in the IR spectrum. The  $T_g$  of the  $\text{CCl}_4$ -insoluble residue versus Ti(OBu)<sub>4</sub> content (Fig. 9) passes through a minimum, thus indicating the maximum PCL quantity becoming attached to this fraction through reactive processing. The minimum  $T_g$  value at 0.15% Ti(OBu)<sub>4</sub> confirms the data shown in Figure 8.

The Ti(OBu)<sub>4</sub> presence during the melt processing enhances formation of bonds connecting PCL and PC chains, probably due to catalysis of ester-carbonate transesterification. Depending on the

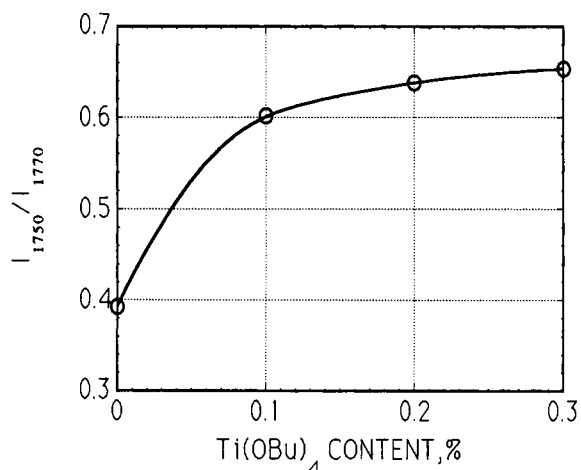


**Figure 8** Effect of Ti(OBu)<sub>4</sub> content on the 70 : 30 PC-PCL blends'  $\text{CCl}_4$  solubility and on  $\text{CCl}_4$  insoluble residue composition.



**Figure 9** Effect of Ti(OBu)<sub>4</sub> content on  $T_g$  of the 70 : 30 PC-PCL blends'  $\text{CCl}_4$  insoluble residue.

catalyst concentration, the copolymer macromolecules containing alternating PC and PCL sequences of different lengths are produced. At low catalyst concentrations, block-copolymer chain formation takes place, resulting in reduced blend solubility in  $\text{CCl}_4$  and some PCL containing insoluble residue. At higher catalyst concentrations shorter sequences and enhanced random-block distribution are obtained. Since prolonged melt mixing (more than 30 min) of PC with PCL at  $240^\circ\text{C}$  has also resulted in increased insoluble fraction, the role of catalyst concentration is indeed just to accelerate the chain randomization process.<sup>7,13</sup> Beyond 0.2% Ti(OBu)<sub>4</sub>, short PC sequences, contained in PCL-rich copolymer chains, are transferred into the  $\text{CCl}_4$ -soluble fraction, explaining the minimum shown in Figure 8. Branching reactions<sup>16</sup> could also be considered as a reason of the two polymers' "connectedness." The Ti(OBu)<sub>4</sub> role in this case would be to accelerate the branching formation. However, the 70 : 30 PC-PCL blends'  $\text{CCl}_4$  solubility increase observed in blends containing more than 0.15% Ti(OBu)<sub>4</sub> can hardly be explained in terms of branched structure formation. While the  $\text{CCl}_4$  solubility dependence on the Ti(OBu)<sub>4</sub> catalyst content shows a minimum solubility, the IR spectra of the PC-PCL-Ti(OBu)<sub>4</sub>-reactive blends show a continuous increase in the absorbance between  $1730$  and  $1770\text{ cm}^{-1}$  as the Ti(OBu)<sub>4</sub> content increases (Fig. 10). It should be noticed that since dilute polymer solutions were tested, the latter FTIR results cannot be related to any solid-state changes of individual polymers, as previously reported.<sup>20</sup> This continuously increased absorbance could stem from the appearance of new absorption bands associated with stretching of mixed aromatic-aliphatic carbonate and ester car-



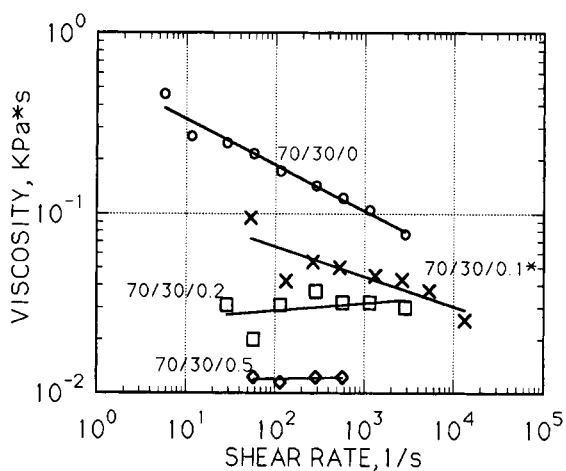
**Figure 10** IR relative absorption intensity changes in the 70 : 30 PC-PCL blends as affected by  $\text{Ti}(\text{OBu})_4$  content.

bonyls. Attempts to separate these bands have not been successful at present.

Melt viscosity decreases and the melt flow behavior of the 70 : 30 PC-PCL blends becomes more Newtonian as the  $\text{Ti}(\text{OBu})_4$  content increases (Fig. 11). Similar to the PC-PCL-*p*-TSA blends, repeated CO—O bond breaking and redistribution in the presence of  $\text{Ti}(\text{OBu})_4$  lead to shorter chains with more uniform molecular weight distribution resulting in the viscosity reduction.

### Organotin Catalyst

Being very active in catalyzing transesterification,  $\text{Ti}(\text{OBu})_4$  causes significant blend discoloration due to complexation with phenolic end groups of PC,<sup>11</sup> and it also accelerates other side reactions during



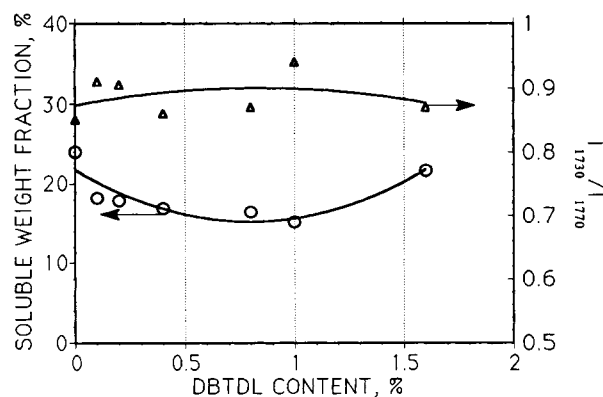
**Figure 11** Melt rheology of PC-PCL- $\text{Ti}(\text{OBu})_4$  blends.

melt processing.<sup>7</sup> In addition, being extremely moisture sensitive,  $\text{Ti}(\text{OBu})_4$  is not easy to handle. From the foregoing points of view organotin compounds may be preferable to  $\text{Ti}(\text{OBu})_4$ .

Brabender plastograph mixing experiments of 70 : 30 PC-PCL blends with added DBTDL were prepared as previously described. The tin catalyst concentration was varied in the range 0–1.6%. Neither melt discoloration nor significant foaming was observed during melt blending. Unlike the  $\text{Ti}(\text{OBu})_4$ -treated blends, the 70 : 30 PC-PCL blends, processed in the presence of DBTDL, were opaque, similar to their physical 70 : 30 PC-PCL counterpart blend.

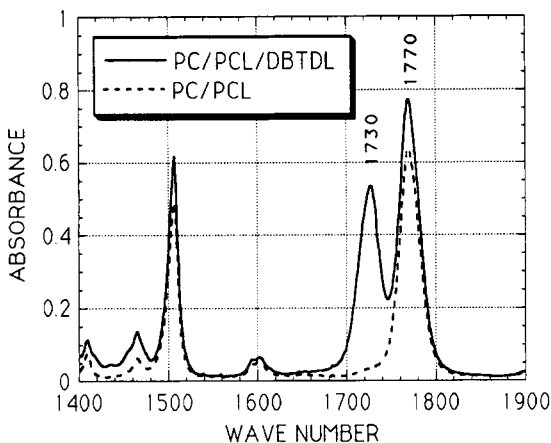
The DBTDL effect on the 70 : 30 PC-PCL blends'  $\text{CCl}_4$  solubility and insoluble residue composition is shown in Figure 12. The quantity of soluble weight fraction and apparently also the PCL relative content in the insoluble fraction (relative  $1730\text{ cm}^{-1}$  band intensity) versus catalyst concentration pass through an extremum at about 0.8% DBTDL. Qualitatively, this behavior is similar to that observed with  $\text{Ti}(\text{OBu})_4$ , but both the solubility minimum and PCL content maximum are less pronounced in this case. Thus, DBTDL is less effective as a catalyst for ester-carbonate exchange reactions than  $\text{Ti}(\text{OBu})_4$  but has some advantages, as previously described.

Melt processing of the 70 : 30 PC-PCL physical blend and 70 : 30 : 1 PC-PCL-DBTDL-reactive blend was done using a single-screw extruder. The  $\text{CCl}_4$ -soluble weight fractions found were 34 and 16% for the physical and reactive blends, respectively. IR spectra of the insoluble blend residues are compared in Figure 13. A strong band at  $1730\text{ cm}^{-1}$ , present in the reactive blend residue spectrum, is completely undetectable in the spectrum of the



**Figure 12** Effect of DBTDL content on 70 : 30 PC-PCL blends'  $\text{CCl}_4$  solubility and on  $\text{CCl}_4$  insoluble residue composition.





**Figure 13** IR spectra of the  $\text{CCl}_4$  insoluble residues.

physical blend. Evidently, the reduced residence time in extrusion processing is sufficient only for the catalyzed reactions to proceed, but not the thermally induced ones. DBTDL appears to be potentially active to catalyze ester-carbonate interchange reactions in reactive extrusion processing. Since reactive extrusion, rather than reactive batch blending, is the preferred processing method, its practical potential calls for future investigations.

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