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Catalyst effect on the transesterification reactions between polycarbonate and polycaprolactone-B-polydimethylsiloxane triblock copolymers

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Summary

Transesterification reactions between bisphenol-A polycarbonate and polydimethylsiloxane-polycaprolactone block copolymers were studied in melt at 270°C. Influence of the composition of reaction mixture and the catalyst type on the formation and properties of the products obtained were investigated by spectroscopic, chromatographic and thermal methods. Both of the catalysts used, zinc acetate and lanthanum acetylacetonate are very efficient transesterification catalysts for the system studied. GPC and DSC results clearly show the formation of novel polymers displaying combined properties of the polycarbonate and the silicone-ester copolymer.

Introduction

Polydimethylsiloxane (PDMS) containing multiphase organic copolymers display a unique combination of bulk and surface properties depending on their chemical compositions and macromolecular architectures(1,2). This is usually due to very good phase separation between nonpolar PDMS and moderately or highly polar organic segments present in these systems(3). The surfaces of films, fibers or other articles prepared from these copolymers by solvent casting or melt processing are also predominantly covered with PDMS, which has a very low surface energy (21-22 mN/m)(1,4). As a result, depending on the nature and properties of the organic blocks, copolymer composition and PDMS block lengths, it is possible to obtain block copolymers with very good mechanical strength, low temperature flexibility and toughness, water repellancy and biocompatibility(1,3,5).

Preparation of siloxane containing block copolymers are usually achieved through the solution polymerization of α,ω-organofunctionally terminated PDMS oligomers and respective difunctional organic monomers or oligomers(1,3). Bulk copolymerization, is usually not very suitable due to complete immiscibility between PDMS and most organic monomers and oligomers even in melt(1).

Polycarbonates (PC) are one of the most important classes of engineering thermoplastics with excellent optical properties, impact tolerance, processability and moderately high Tg and thermal stability. On the other hand they have poor low temperature impact strength and more importantly very poor resistance to many organic solvents, which usually leads to catastrophic failure, especially when the system is under mechanical stress. It is possible to improve the stress crack resistance of PC by surface modification. PC-PDMS segmented copolymers show

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substantial improvements in stress crack resistance, since surfaces of these systems are mainly composed of PDMS(1,3). Solvent cast films of PC-PDMS also display excellent clarity and good mechanical and thermal properties and find applications as biomaterials and membranes. These copolymers also display excellent low temperature impact properties much superior to that of pure PC.

PC-PDMS segmented copolymers are usually produced by phosgenation of bisphenol-A and α,ω-dichloro(6), α,ω-dimethylamino(7) or α,ω-hydroxyaryloxy(8) terminated PDMS oligomers in solution. High molecular weight PC-PDMS copolymers can also be obtained by a interfacial polycondensation in a two phase aqueous/organic solvent system. Although these techniques are commonly used even in commercial production, the new trend is towards solvent-free polymerizations, which is both environmentally friendly and also more economical. There is only one study available in the open literature on the melt polycondensation between PC and PCL-PDMS-PCL, with very limited information on the reaction mechanism and product characteristics(9).

In this study melt transesterification between polycarbonate and a polycaprolactone-PDMS block copolymer was investigated for the preparation of PC-PDMS block copolymers. The influence of the type and the amount of catalyst on the extent of transesterification reactions were investigated. Products formed were characterized by FT-IR spectroscopy, gel permeation chromatography (GPC), differential scanning calorimetry (DSC) and thermogravimetric analysis (TG).

Experimental

Materials

Poly(bisphenol-A carbonate) was a product of Bayer AG. GPC analysis (based on polystyrene standards) yielded Mn and Mw values of 24,500 and 44,500 g/mole respectively.

Polycaprolactone-polydimethylsiloxane-polycaprolactone (PCL-PDMS-PCL) triblock copolymer was kindly supplied by Goldshmidt. Chemical Corporation, Hopewell, VA, USA. PCL and PDMS block molecular weights were 2,000 and 3,000 g/mole respectively, with an Mn value of 7,000 g/mole. It contained 300 ppm of organotin catalyst, which is used during polymerization(10). GPC analysis of this product yielded Mn and Mw values of 11,000 and 17,000 g/mole respectively. Melting point of PCL blocks was determined to be 60°C by DSC. Transesterification catalysts used in this study were zinc acetate [$Zn(Ac)_2.2H_2O$] and lantanium acetylacetonate [$La(Acac)_3$], which were obtained from Aldrich. Solvents, chloroform (Merck), tetrahydrofuran (Fluka), carbontetrachloride (Fluka) were all reagent grade and were used as received.

Experimental procedure

Melt polycondensation reactions between PC and PCL-PDMS-PCL were carried out in a laboratory scale Haake high-shear mixer consisting of a heating chamber (50 g total capacity) with two counterrotating screws. PC was dried at 120°C overnight to remove moisture before blending. PCL-PDMS-PCL was used as received. During the experiments PC was first fed into the mixing chamber preheated to 270°C and processed until a clear melt was obtained. Desired amounts of PCL-PDMS-PCL and catalysts (weight% based on the PC content of the mixture) were then added into the system. Immediately after addition, due to very low melting point of PCL blocks PDMS copolymer melted. This resulted in a dramatic reduction in the torque, which is due to very well known lubricating effect of silicones. However, molten polymer mixture showed a clear phase separation between more viscous PC phase and liquid like PCL-PDMS-PCL. Depending on the composition of the mixture and the amount of catalyst, the molten blend became homogeneous (with a milky white appearance) within 10 to 50 minutes of mixing. During the reactions the temperature was kept constant at 270°C and the screw speed was maintained at 50 rpm. Samples were taken out of the mixture at different reaction times for characterization.

Characterization methods

FT-IR spectra of the products were recorded on a Nicolet Impact 400D spectrometer using solvent (THF) cast thin films on KBr discs.

DSC measurements were carried out on a Shimadzu DSC-41 model apparatus at a heating rate of 10°C/min under nitrogen atmosphere with a flow rate of 30mL/min. 5-15 mg samples were heated from room temperature to 250°C followed by slow cooling to ambient temperature in the first scan. Melting points (Tm) was defined as the minimum of the DSC endotherm. Heat of fusion (ΔH_f) values were obtained from the area under the peak. Temperature and enthalpy calibration of the instrument was obtained by standard indium, lead and zinc samples.

A Shimadzu TGA-50 was used to determine the thermal stabilities of products. Experiments were carried out under dry nitrogen at a flow rate of 30mL/min and a heating rate of 10°C/min up to 600°C. The temperature of maximum rate of polymer degradation (PDT) was taken as the temperature at which differential thermal gravimetry (DTG) curves reach their maxima.

Carbontetrachloride (a selective solvent for PCL-PDMS-PCL) was used to fractionate the products obtained after transesterification reactions. For this purpose samples with known weights (W_t) were extracted for 24 hours at room temperature. Soluble fractions were removed by filtration. Insoluble polymer was dried at 120°C until constant weight (W_2). The degree of solubility was determined by the ratio (W_t-W_2)/W_t.

GPC studies were carried out on a Polymer Laboratories PL-GPC 110 equipped with microstyragel columns of 500, 1000 and 10,000A and a refractive index detector. Measurements were done at 23°C, in THF with a flow rate of 1mL/min. Calibration curve was obtained by using polystyrene standards.

Results and discussion

For technical and economical reasons reactive blending provides a convenient route for the preparation of new polymeric materials from already existing systems. Transpolymer reactions that take place during melt blending can be used to modify the chemical structures and/or to improve compatibility between polymers which are otherwise immiscible. This approach is particularly attractive in the case of polycondensates such as polyamides, polyesters, polyurethanes and polyureas, which contain a large number of reactive groups in their backbone structures.

In this investigation we studied the influence of catalyst type on the reactive blending of PC with PCL-PDMS-PCL triblock copolymer. Although transesterification reactions between PC and many polyesters, including PCL have been extensively investigated, reactions of PC with a polyester block copolymer have not been studied.

Table 1 gives the detailed description of the reaction systems, together with the results of GPC experiments. As can be seen from this Table, two different PC to siloxane copolymer ratios, 80/20 and 50/50 were investigated. The catalysts were employed at a fixed concentration of 0.5% by weight (based on PC weight). Reaction times were varied between 30 and 60 minutes. Control experiments were also conducted on PC with and without catalyst and on some blends without any added catalyst.

Table 1. Compositions of polycarbonate/PCL-PDMS-PCL blends and GPC results on the reaction products

Sample Composition	Catalyst Type	Catalyst Amount	Reaction Time (min)	Mn (g/mole)	Mw (g/mole)
PC	–	–	–	25,500	44,500
PC	–	–	30	25,000	44,500
PC	–	–	60	25,000	43,000
PC	Zn	0.5	30	15,000	26,500
PC	Zn	0.5	60	11,500	22,000
PC	La	0.5	60	13,000	26,000
PCL-PDMS-PCL	–	–	–	11,000	17,000
80PC/20	–	–	30	24,500	44,500
80PC/20	–	–	60	22,500	40,500
80PC/20	Zn	0.5	30	16,500	37,500
80PC/20	Zn	0.5	60	12,500	23,500
80PC/20	La	0.5	30	14,000	26,500
80PC/20	La	0.5	60	11,500	22,500
50PC/50	–	–	30	16,000	30,000
50PC/50	–	–	60	15,000	27,500
50PC/50	Zn	0.5	30	13,000	28,000
50PC/50	Zn	0.5	60	11,500	24,500
50PC/50	La	0.5	30	12,500	25,500
50PC/50	La	0.5	60	9,000	20,500

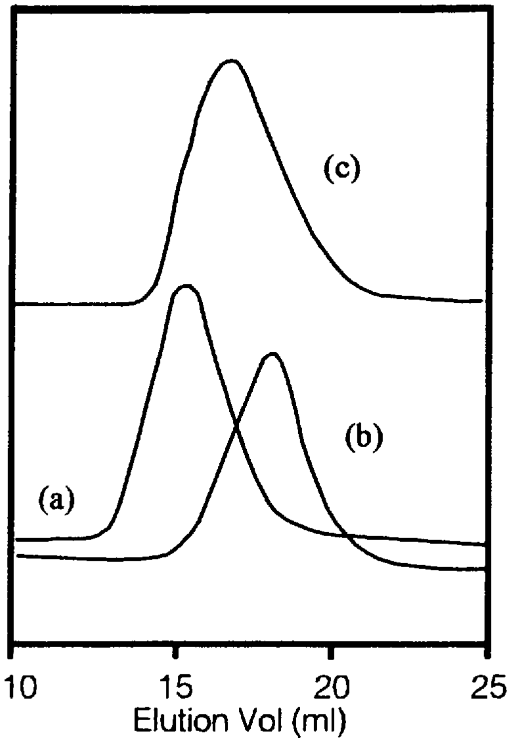

Fig.1. GPC curves for PC, PCL-PDMS-PCL and their 50/50 blends before melt processing
(a) PC
(b) PCL-PDMS-PCL
(c) 50/50 blend

From control experiments on PC it is clear that when processed for 30 or 60 minutes at 270°C, without any catalyst, no noticeable change was observed in the Mn or Mw values of PC. On the other hand, as can clearly be seen in Table 1, with the addition of small amounts of $Zn(Ac)_2$ or $La(Acac)_3$ a dramatic reduction in both Mn and Mw of pure PC were observed. Therefore, it is clear that both catalysts are very effective in cleaving the carbonate bond.

GPC chromatograms of pure PC, PCL-PDMS-PCL and their 50/50 blends without any external catalyst, before processing at 270°C, are given in Fig. 1. In 50/50 blend there is a low molecular weight tail in the GPC curve (Fig. 1(c)). In 50/50 blends processed for 30 and 60 minutes at 270°C without the addition of any external catalysts, there is indication of some transesterification reaction taking place between two polymers based on GPC results and FTIR studies. This is due to the presence of about 300 ppm of an organotin catalyst present in PCL-PDMS-PCL copolymer. If no transesterification reaction has taken place, expected Mn and Mw for 50/50 blend would have been 18,250 and 36,500 g/mole respectively. On the other hand as given on Table 1, GPC data yields Mn and Mw values of 16,000 and 30,000 g/mole for 50/50 blend melt processed for 30 minutes without any added catalysts, indicating a very small extent of reaction. As indicated in the literature(10, 11) and also observed in this study, organotin compounds are efficient catalysts for the ring-opening polymerization of caprolactone, however, not as powerful for the transesterification reactions.

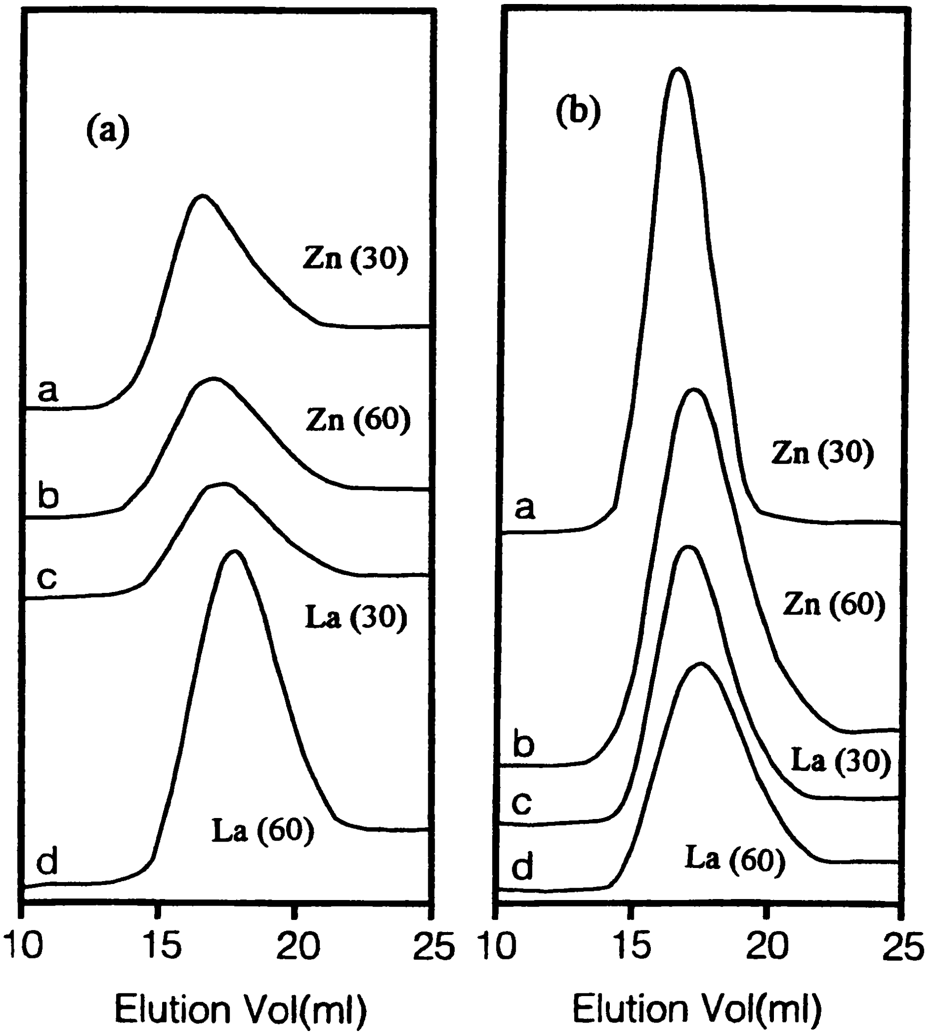

Fig. 2. GPC curves for PC/PCL-PDMS-PCL blends after processing with 0.5% by weight $Zn(Ac)_2$ and $La(Acac)_3$ catalysts
(a) 80PC/20 blend
(b) 50PC/50 blend

On the other hand both zinc acetate and lanthanum acetylacetonate are very powerful catalysts as transesterification catalysts for polycarbonate/polydimethylsiloxane-polycarbonate system. As can be seen on Table 1, when 0.5% by weight of catalyst is employed, both in 80PC/20 and 50PC/50 blends, after 30 minutes of reaction there are substantial reductions in Mn and Mw values. These indicate both a large extent of transesterification reactions in these systems and also some degradation reactions. GPC curves for these samples are reproduced in Fig. 2.

Table 2 provides the results of the solubility tests in carbontetrachloride, a selective solvent for the silicone-caprolactone copolymer. As expected, pure PC did not show any solubility in carbontetrachloride even after 60 minutes of melt processing with 0.5% $Zn(Ac)_2$ or $La(Acac)_3$ catalysts. In 80PC/20 blends, after 30 minutes of reaction without any added catalyst, soluble fraction was determined to be 28%, which is slightly higher than expected, if no transesterification reaction has taken place. As explained before, organotin catalysts present in the silicone copolymer leads to some reaction in the system. The product formed is rich in silicone copolymer which results in higher solubility. After 60 minutes of reaction the soluble fraction goes down to 17% indicating that system has been randomized and dominated by PC, which is insoluble in carbontetrachloride.

Table 2. Product solubilities in Polycarbonate/PCL-PDMS-PCL blends after transesterification reactions

Sample Composition	Catalyst Type	Catalyst Amount	Reaction Time (min)	Soluble fraction (Weight %)
PC	–	–	–	–
PC	Zn	0.5	30	–
PC	Zn	0.5	60	–
PC	La	0.5	60	–
PCL-PDMS-PCL	–	–	–	100
80PC/20	–	–	30	28
80PC/20	–	–	60	17
80PC/20	Zn	0.5	30	40
80PC/20	Zn	0.5	60	14
80PC/20	La	0.5	30	13
80PC/20	La	0.5	60	13
50PC/50	–	–	30	31
50PC/50	–	–	60	33
50PC/50	Zn	0.5	30	100
50PC/50	Zn	0.5	60	100
50PC/50	La	0.5	30	100
50PC/50	La	0.5	60	100

These results are strongly supported by FTIR observations. Fig.3-a gives the FTIR spectra of the carbonyl region for pure PC and pure PCL-PDMS-PCL. PC shows a strong carbonyl absorption peak at 1774 cm^{-1}, whereas PCL-PDMS-PCL shows aliphatic ester carbonyl at 1727 cm^{-1}. Fig.3-b and Fig.3-c give the FTIR spectra of carbontetrachloride soluble and insoluble fractions of 80PC/20 and 50PC/50 blends respectively, which were melt processed for 60 minutes without any added catalyst. It is clear that after 60 minutes of processing, due

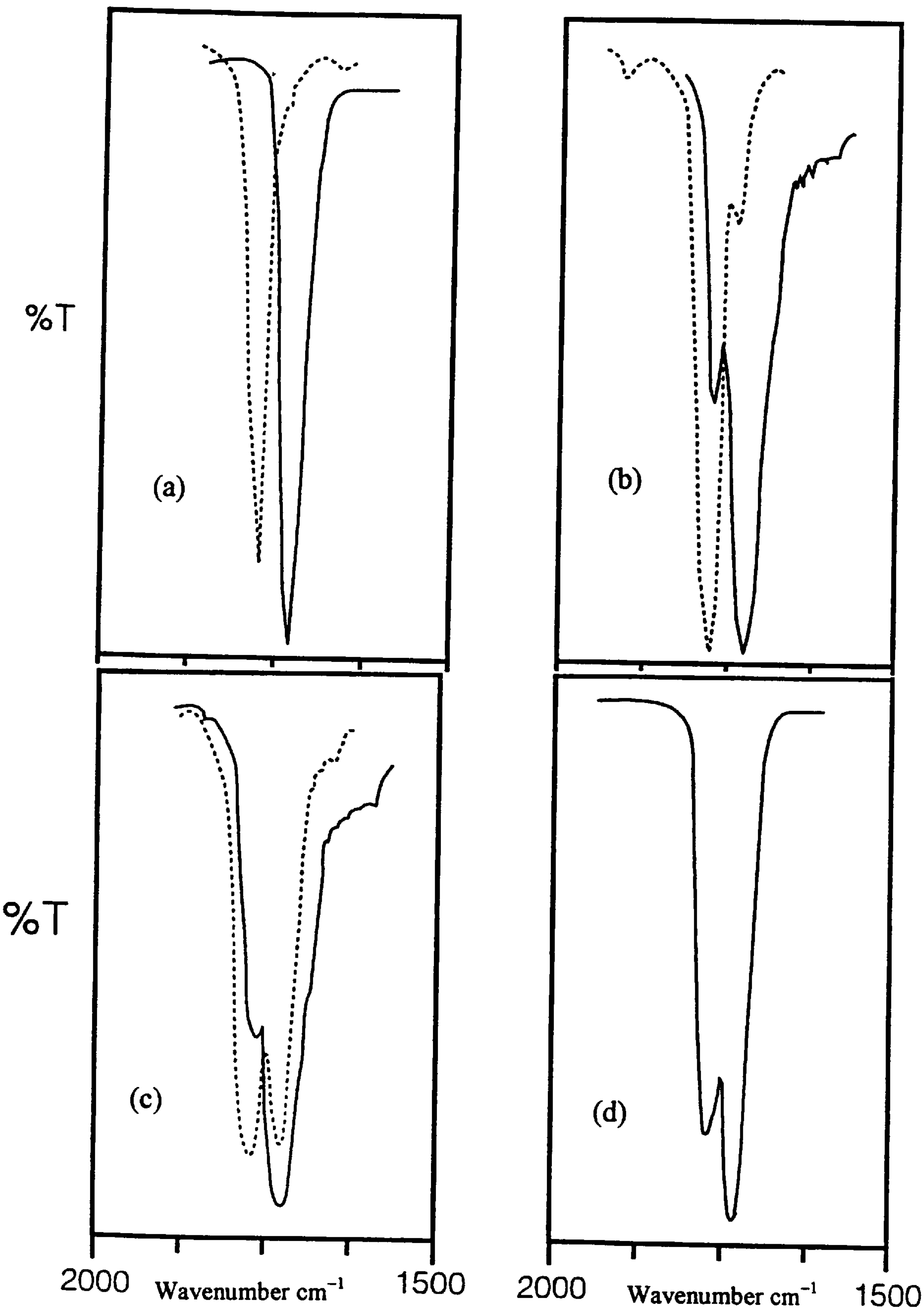

Fig. 3. FTIR spectra of (a) PC (-----) and PCL-PDMS-PCL (———) (b) CCl_4 insoluble (-----) and soluble (———) fractions of 80PC/20 blends after processing (c) CCl_4 insoluble (-----) and soluble (———) fractions of 50PC/50 blends after processing (d) 50PC/50 blends after processing with 0.5% by weight $Zn(Ac)_2$ catalyst for 30 minutes.

to the presence of very small amount of organotin catalyst in the silicone-ester copolymer, transesterification reaction takes place in both of the blends. This is evidenced by the presence of PC and PCL carbonyl peaks in both the carbontetrachloride soluble and insoluble fractions. Characteristic Si-O-Si stretching peaks for PDMS are also observed between 1000 and 1100 cm^{-1} as a broad doublet in both soluble and insoluble fractions. However, randomization is imcomplete, since especially in 50PC/50 blends fully randomized systems show complete solubility in carbontetrachloride. This can be achieved by using both zinc or lanthanum based catalysts, as clearly shown in Table 2. FTIR spectrum of 50PC/50 sample processed under 0.5% zinc acetate catalysts for 30 minutes is reproduced in Fig.3-d. This material shows complete randomization, which is clearly indicated by the relative sizes of the two carbonyl peaks in the spectrum.

All of these results were also supported by the results of our thermal analysis studies on the starting materials and the products obtained. Results of these investigations carried out by differential scanning calorimetry and thermogravimetric analyses are being prepared for publication.

Conclusions

Influence of organometallic catalysts such as zinc acetate and lanthanum acetyl acetonate were investigated on the melt transesterification reactions between polycarbonate and polycaprolactone-b-polydimethylsiloxane triblock copolymers. Solubility studies in selective solvents, GPC investigations and FTIR identification of the products all indicate that zinc acetate and lanthanum acetylacetonate are very effective transesterification catalysts for the system studied.

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