

Synthesis and Characterization of Soluble Polyester Based on Calixarene Dicarboxylic Acid with Tertiary Butyl Pendant Groups

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Abstract A series of new polycalixesters (PCES) were synthesized by polyesterification of calixarene dicarboxylic acid derivatives having tertiary butyl pendant groups at the upper rim using five different diols. All polyesters were readily soluble in polar solvents such as NMP (*N*-methylpyrrolidone), DMF (dimethylformamide), DMSO (dimethylsulfoxide), pyridine, THF (tetrahydrofuran), HMPA (hexamethylenephosphoramide) and DMAC (dimethylacetamide). The PCES were also partially soluble in TCE (tetrachloroethane) and ethanol and they were insoluble in acetone. The glass transition temperatures of polyesters were between 80–184 °C, the crystallinity temperatures of polyesters were between 130–212 °C and the melting temperatures of polyesters were between 185–234 °C, as determined by differential scanning calorimeter (DSC). The inherent viscosities of polyesters were obtained from 0.55 dL/mg to 0.61 dL/mg. The temperatures at 10% weight loss of polyesters ranged from 182 °C to 237 °C. The temperatures at 25% weight loss of polyesters ranged from 258 °C to 331 °C. The half weight loss (50%) temperatures of polyesters were among 315 °C to 371 °C and the char yields at 600 °C were determined within 13% to 22.3% in N₂ atmosphere, as determined by thermo gravimetric analysis (TGA). The polyester, PES3, has the higher melting point (234 °C) and higher inherent viscosity (molecular weight) than the other polyesters.

Keywords: Calixarene; Polyester; Thermal stability; TGA; DSC.

INTRODUCTION

Aromatic polyesters such as poly(ethylene terephthalate) (PET), poly(butylene terephthalate) (PBT), poly(ethylene naphthalate) (PEN) and the recently introduced poly(trimethylene terephthalate) (PTT) have taken a central position under engineering plastics. As fiber, bottle and film material or as matrix for glass-reinforced plastics, they have found a wide field of application. Aliphatic polyesters derived from dicarboxylic acids and 6-dihydroxyalkanes are known since the pioneering work of Carothers^[1, 2]. Aromatic polyesters have found a wide range of applications due to their remarkable properties such as good heat and chemical resistance, low shrinkage, low water content, good barrier properties and interesting physico-mechanical properties. However, limitations arise from their high melting temperature and limited solubility in most organic solvents^[3–5]. A number of thermally stable aromatic polyesters^[6–8], different polyesters^[9–11] and aromatic polyesters^[12–15] have been prepared previously. In an earlier report^[16] the synthesis of hexa-*tert*-butylhydroquinone) cyclotriphosphazene (tbuHQCP) were described. This cyclotriphosphazene was formed with regioselectivity with the *tert*-butyl group positioned away from the inorganic ring. Additionally, this cyclotriphosphazene exhibited no oligomerization due to reaction with both hydroxyls of *tert*-butylhydroquinone, as opposed to syntheses reported using simple hydroquinone^[17]. The preparation of poly(L-lactide-*b*-DXO-*b*-L-lactide) has

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recently been reported using controlled ROP in a two-stage process: polymerization of DXO using a difunctional initiator: 1,1,6,6-tetra-*n*-butyl-1,6-distanna-2,5,7,10-tetraoxacyclodecane, and the addition and polymerization of L-lactide in chloroform at 60 °C^[18]. Beside these studies to prepare better and more applicable polyesters, using supramolecular structures in the polymeric backbone such as calixarene moieties which are known in supramolecular systems as outstanding organic compounds that have drawn extensive utility since their first preparation and characterization by Gutsche *et al.*^[19] has great impacts on the polymer characteristics. Due to the hydroxy functionality on the calixarenes, esterification and etherification are the most common approaches which result in various applications of calixarenes especially in chromatography, catalysis, purification, enzyme mimics, ion selective electrodes, phase transfer, transport across membranes, ion channels and self-assembling monolayers^[22–24]. With these amazing capabilities, employing this structure with such a valuable effect such as increasing solubility and decreasing T_g s, can lead to produce more applicable polymers from the industrial point of view.

In this article, and in continuation of our last investigations in preparation of polycalixarenes^[25], we describe the synthesis and characterization of a new diacid containing tertiary butyl pendant groups and polyesters resulting from polycondensation of the diacid with five different diols. The 5, 11, 17, 23-tetra-*tert*-butyl-25, 27-dicarboxy-26,28-dimethoxy calix[4]arene was synthesized using 5,11,17,23-tetra-*tert*-butyl-25,27-diethoxycarbonylmethoxy-26,28-dimethoxycalix[4]arene in the presence of ethanol. The purpose of this investigation is to prepare polyesters containing tertiary butyl groups as pendant groups with improved solubility. The solubility, inherent viscosity, elemental analysis and thermal properties of the polyesters were measured.

EXPERIMENTAL

Materials and Instruments

Pyridine, thionyl chloride and all other chemicals were purchased from Fluka (Switzerland). ¹H-NMR spectra were recorded on a Bruker Aavance DRX 500 MHz instrument, using DMSO-*d*₆ as solvent and tetramethyl silane as an internal standard. FTIR spectra were recorded on a Bruker, Vector 22 spectrometer, using KBr pellets. The CHN-600 Leco analyzer was used for elemental analysis. Thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed at 10 K/min under N₂ atmosphere by using a Perkin-Elmer Pyres and a Metler Toledo 822°, respectively. Inherent viscosity ($\eta_{inh} = \ln \eta_{rel}/c$) of polymers were determined for solution of 0.5 g/dL in NMP at 25 °C using an Ubbelohde viscometer.

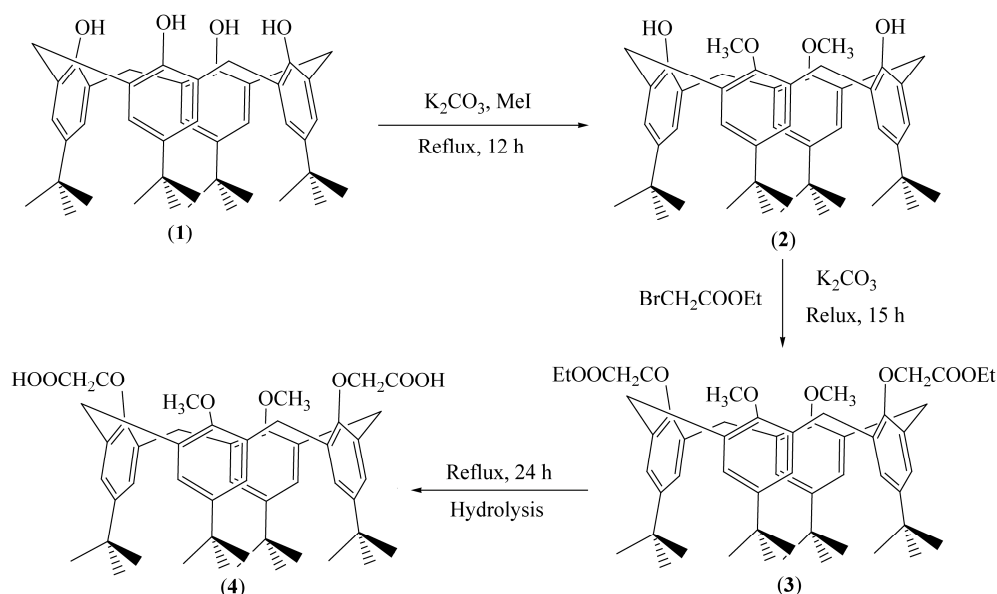
Monomer Synthesis

Synthesis of 5,11,17,23-tetra-*tert*-butyl-25,27-diethoxycarbonylmethoxy-26,28- dimethoxycalix[4]arene (**3**)

The parent calixarene has been synthesized according to Gutsche *et al.* procedure published in literature^[26]. Also, 5,11,17,23-tetra-*tert*-butyl-25,27-diethoxycarbonylmethoxy-26,28-dimethoxycalix[4]arene (**3**) was prepared from the corresponding dimethyl ether calix[4]arene (**2**) according to the previously reported procedure^[27]. The synthetic pathways including substrate, reagents, solvents and reaction conditions are given in Scheme 1.

Preparation of 5, 11, 17, 23-tetra-*tert*-butyl-25, 27-dicarboxy-26,28-dimethoxy calix[4]arene (**4**)

To a solution of **3** (5.00 g, 6.31 mmol) in ethanol (200 mL) was added NaOH (0.8 g, 20 mmol). The mixture was stirred and heated under reflux condition for 24 h. After completion of the reaction which was monitored by TLC, the solvent was distilled off in vacuo. The precipitate was diluted by water (200 mL), and 3 mol/L hydrochloric acid (50 mL) was added with vigorous stirring to reach pH = 1. Then, it was filtered and the pale yellow solid was dried in air. The precipitate was dissolved in chloroform (150 mL) and washed three times with 1 mol/L HCl solution, brine and finally with water respectively. The clear chloroform solution was charged to Heidolph rotavac evaporator to obtain the pure dicarboxylic acid (**4**) in 95% yield.



Scheme 1 The procedure for the preparation of monomer

IR (KBr) cm^{-1} : 3422 (OH), 2957 (C—H aromatic), 1734 (C=O), 1482 (C=C aromatic).

Elemental analysts for $\text{C}_{50}\text{H}_{64}\text{O}_8$ (%): Calcd: C, 75.75; H, 8.08; O, 16.16; Found: C, 75.48; H, 7.79; O: 16.37.

Polymer Synthesis

PES3: The PESs were prepared by the following procedure: For synthesis of polymer PES3, pyridine (0.5 mL) was added to a cold thionyl chloride (0.05 mL, 0.80 mmol) in an ice-water bath, the mixture was kept at this temperature for 10 min. The diacid solution, (0.2 g, 0.37 mmol) in Py (0.5 mL), was added slowly for 10–20 min and then the cooling bath was removed, and the reaction mixture was stirred at room temperature for 30 min. 4, 4'-Dihydroxybiphenyl (**3**) (0.069 g, 0.37 mmol) in Py (0.5 mL) was added to the mixture all at once, and the whole solution was heated at 80 °C for 4 h. Then the viscous liquid was precipitated in 40 mL of methanol to yield 0.20 g (89.2%) of the polymer (PES3). The solubility and inherent viscosity of the prepared polyesters are shown in Table 1. The other polyesters were prepared according to the above method, instead of 4, 4'-dihydroxybiphenyl, we have used bisphenol A for PES1, 4, 4'-dihydroxy-keto-biphenyl for PES2, hexafluoro bisphenol A for PES4 and 4, 4'-dihydroxyphenyl sulfone for PES5.

Table 1. Solubility^a and inherent viscosity of polyesters

Polymer code	NMP	DMF	DMSO	TCE	THF	H ₂ SO ₄	DMAC	Aceton	EtOH	η_{inh}^b (dL/g)
PES1	+	+	+	±	+	+	+	—	±	
PES2	+	+	+	±	+	+	+	—	±	0.58
PES3	+	+	+	±	±	+	±	—	±	0.61
PES4	+	+	+	±	+	+	+	—	±	0.55
PES5	+	+	+	±	+	+	+	—	±	0.55

^a 50 mg polymer in 10 mL solvent at room temperature, soluble (+), partially soluble (±), insoluble (—)

NMP = *N*-methylpyrrolidone, DMF = dimethylformamide, DMSO = dimethylsulfoxide, TCE = tetrachloroethane, Py = pyridine, THF = tetrahydrofuran, HMPA = hexamethylenephosphoramide, DMAC = dimethylacetamide;

^b Measured at 25 °C in NMP

RESULTS AND DISCUSSION

5,11,17,23-tetra-*tert*-butyl-25,27-dicarboxy-26,28-dimethoxy calix[4]arene (**4**) was synthesized according to the procedure published in the literature^[25, 26]. FTIR and melting point were used to confirm the structures of the compounds which were in good agreement with those given in the literatures. Scheme 1 displays the structure of the starting material. FTIR spectrum of diacid compound showed characteristic IR peaks (cm^{-1}) at: 3422 (OH), 2957 (C—H aliphatic), 1734 (C=O) and 1482 (C=C aromatic), and is shown in Fig. 1.

5,11,17,23-tetra-*tert*-butyl-25,27-dicarboxy-26,28-dimethoxy calix[4]arene (**4**) was used as a starting material for the preparation of polyesters in reaction with 5 different diols. The reaction of compound (**4**), (0.37 mmol) with the diol (Ar: **3**) (0.37 mmol) was conducted in 0.5 mL pyridine in the presence of thionyl chloride (0.5 mL), for 10–20 min at 0 °C and for 30 min in room temperature (Scheme 2). The structure of polyester was confirmed by common spectroscopic methods such as FTIR and ^1H -NMR. The FTIR spectrum of the PES3, Fig. 2, shows characteristic peaks at (cm^{-1}): 3422 (OH), 2999 (CH aliphatic), 1747 (C=O), 1480, 1364 (C=C), 1298 (—O—) and 1198–1056 (C—O).

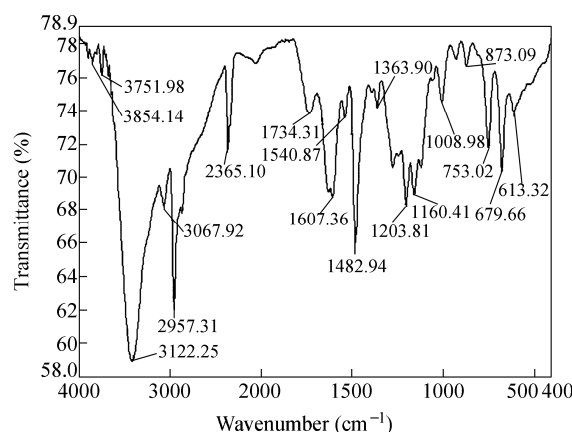
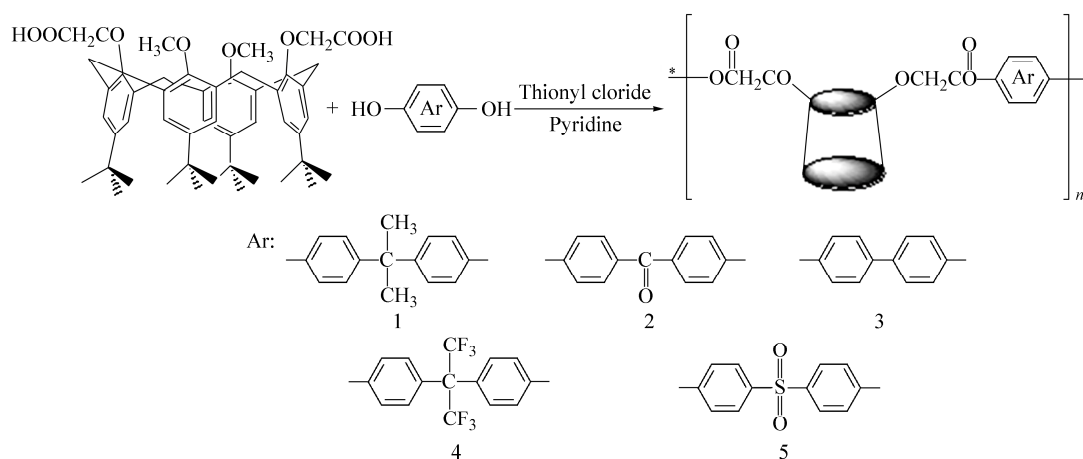


Fig. 1 The FTIR spectrum of diacid



Scheme 2 The typical procedure for the preparation of polyesters

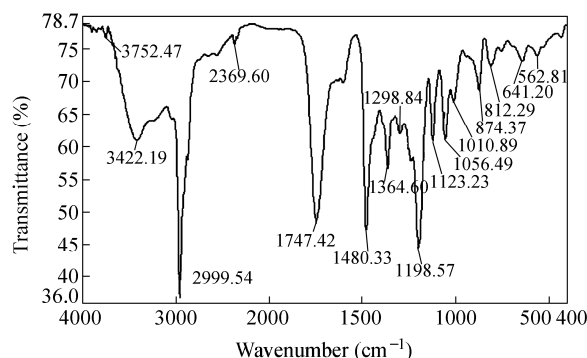


Fig. 2 The FTIR spectrum of PES3

The ^1H -NMR spectrum Fig. 3, shows the characteristic signals of phenolic proton at $\delta = 8.7$, and at $\delta = 6.6$ – 7.7 for aromatic protons, $\delta = 4$ – 4.15 for OCH_2 protons, $\delta = 3.9$ for $\text{O}-\text{CH}_3$ protons and characteristic signals at $\delta = 1.15$ – 1.18 for tertiary butyl protons. The structure of the synthesized polyesters was confirmed by spectroscopic methods. The IR-spectral data (cm^{-1}) of PES3 were 2999 (CH aliphatic), 1747 ($\text{C}=\text{O}$), 1480, 1364 ($\text{C}=\text{C}$), 1250–1120 ($-\text{O}-$) and 1198–1056 ($\text{C}-\text{O}$) and the ^1H -NMR data (δ) of PES3 were 8.7 (phenolic proton), 6.6–7.7 (aromatic proton), 4–4.15 ($\text{O}-\text{CH}_2$), 3.9 ($\text{O}-\text{CH}_3$) and 1.15–1.18 (*t*-butyl proton).

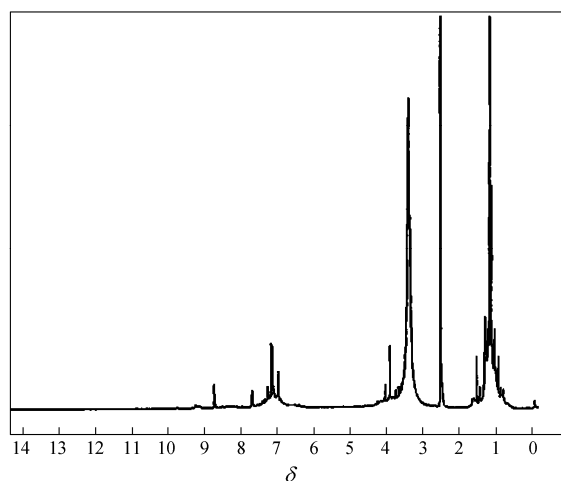


Fig. 3 The ^1H -NMR spectrum of PES3

The inherent viscosity of the polyesters was measured at a concentration of 0.5 g/dL in NMP at 25 °C for the polymerization reaction, and the results are shown in Table 1. Due to the direct relationship between viscosity and molecular weight of polymers it can be concluded that the higher the molecular weight of the polymer the high its viscosity, therefore, the molecular weight of PES3 is higher than that of the others. Typical FTIR and ^1H -NMR spectra of polyesters (PES3) are shown in Figs. 2 and 3. The solubility of polyesters was tested in different organic solvents at room temperatures, and the results are shown in Table 1. The polyesters were very good soluble in organic solvents such as DMF, DMSO except acetone.

Typical DSC thermogram of polyester, PES3, is shown in Fig. 4. The polyesters showed a sharp endothermic peak in the range of 210 °C for PES1(bisphenol A) and 234 °C for PES3 (biphenyl) and a exothermic peak for PES1(bisphenol A) in the range of 280 °C and a exothermic peak for PES3 (biphenyl) in the range of 340 °C. The DSC thermogram showed the glass temperature, the crystallization temperature, the melting temperature and the decomposition temperature of PES1 at 70, 190, 210 and 280 °C respectively and for PES3 at 184, 195, 234 and 340 °C respectively. The DSC curves showed that the crystallization and

decomposition temperature are exothermic and melting points are endothermic. The DSC thermograms of PES3 represents that the glass temperature, the crystallization temperature, the melting temperature and the decomposition temperature of PES3 are higher than those of others, it is because for PES3 there is no substituted groups between two phenyl groups and the two groups are combined to increase the thermal stability. The endothermic peaks in DSC thermograms of polyesters appeared at the same temperature where TGA curves showed a small weight loss.

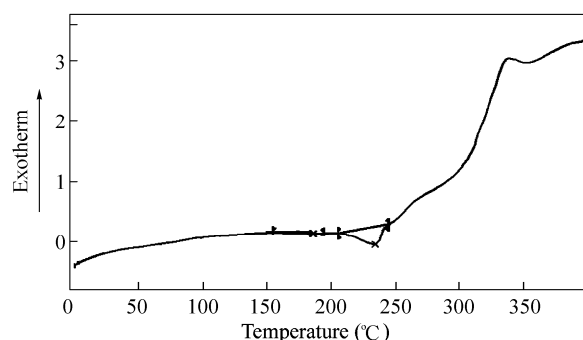


Fig. 4 The DSC curve of PES3

The TGA curve of polyester PES3 is shown in Fig. 5 and the TGA curves of all polyesters are shown in Fig. 6.

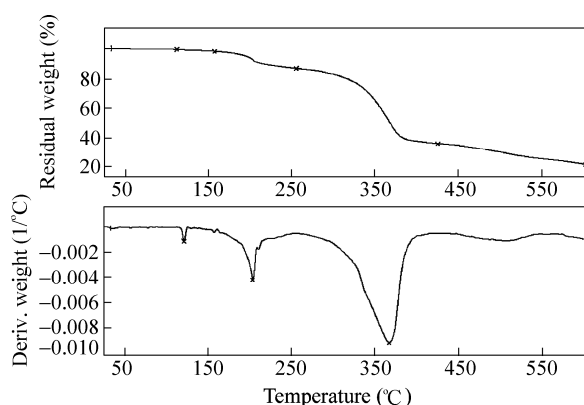


Fig. 5 The TGA curve of PES3

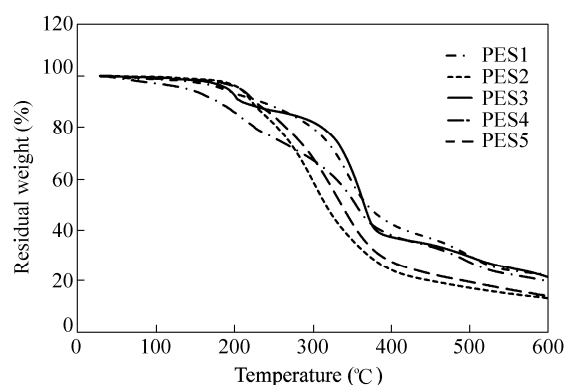


Fig. 6 The TGA curves of PESs

There is a less than 10% weight loss around 182–237 °C. There is about 25% weight loss in the temperature range of 258–331 °C, 50% weight loss in the temperature range of 315–371 °C and then the samples were heated to 600 °C where the weight remained almost in the range of 13%–22.3%. The obtained results are collected in Table 2.

Table 2. The DSC and TGA data of polyesters

Comp.	T_g ¹ (°C)	T_c ² (°C)	T_m ³ (°C)	T_d ⁴ (°C)	$T_{10\%}$ ⁵ (°C)	$T_{25\%}$ ⁶ (°C)	$T_{50\%}$ ⁷ (°C)	Ch. Y. ⁸ (%)
PES1	75	190	210	280	237	320	371	22.3
PES2	110	170	200	220	226	280	340	14
PES3	184	195	234	340	211	331	367	21.4
PES4	92	175	220	309	182	258	357	19.9
PES5	—	—	—	—	221	267	315	13

¹ Glass transition temperature obtained from DSC; ² Crystallization temperature obtained from DSC; ³ Melting temperature obtained from DSC; ⁴ Decomposition temperature obtained from DSC; ⁵ Temperature of 10% weight loss obtained from TGA; ⁶ Temperature of 25% weight loss obtained from TGA; ⁷ Temperature of 50% weight loss obtained from TGA; ⁸ Char yield percent at 600 °C obtained from TGA

CONCLUSIONS

A series of polyesters containing tertiary butyl as pendant groups in the main chain as diacid section were prepared from the reaction with different diols, and the molar ratio of diacid chloride to the diol was 1:1 and the reaction was carried out in ice-water for 10 min and then at room temperature for 30 min. The polyesters were fully characterized and their thermal properties were studied. The introduction of tertiary butyl groups in structure of the diacid resulted in polyesters with very good solubility in aprotic solvents such as NMP, DMF, DMSO, THF, H₂SO₄, DMAC and DMAC. The DSC thermograms of PES3 represents that the glass temperature, the crystallization temperature, the melting temperature and the decomposition temperature of PES3 are higher than those of others, it is because for PES3 there is no substituted groups between two phenyl groups and the two groups are combined to increase the thermal stability. The endothermic peaks (melting temperature) in DSC thermograms (~200 °C) of polyesters appeared at the same temperature where TGA curves showed a small weight loss, and the exothermic peaks (decomposition temperature) in DSC thermograms (~300 °C) of polyesters appeared at the same temperatures where TGA curves showed a high weight loss.

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