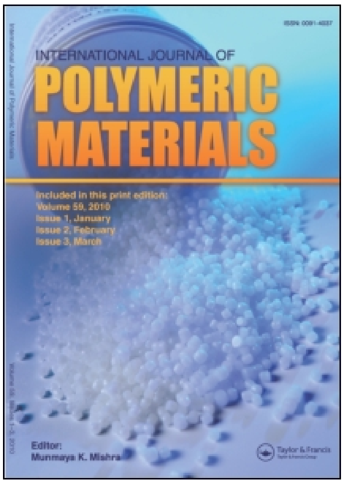

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A. Pourjavadi[a]; M. J. Zohuriaan-mehr[ab]; N. Rezai[a]
[a] Chemistry Dept., Sharif Univ. of Tech., Tehran, Iran [b] Adhesive & Resin Dept., Iran polymer Institute, Tehran, Iran

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Synthesis, Chemical and Thermal Characterization of Poly(*cis*-2-butenylene oxalate)

A. POURJAVADI*, M. J. ZOHURIAAN-MEHR† and N. REZAI

Chemistry Dept., Sharif Univ. of Tech., Box 11365-9516 Azadi Ave., Tehran, Iran

A non-terminated, low molecular weight, highly crystalline, linear aliphatic polyester was successfully synthesized *via* ester-interchange polycondensation of *cis*-2-butene-1,4-diol and diethyl oxalate by using of lead (II) oxide as the catalyst. No decarboxylation occurred during the optimized polymerization. Structural and Chemical identification was performed by elemental analysis, FTIR, ^{1}H-NMR, and Mass spectroscopy. Some macrocycle species were detected in the product, according to GPC. Fragmentation patterns were suggested for the main m/e's of the mass spectrum. Thermal characterization was performed by DSC and TGA. It was found that the overall thermal stability of the polyester is higher than that of the corresponding homologous polyesters.

Keywords: 2-Butene-1,4-diol; polyoxalate; aliphatic polyester; synthesis; transesterification; characterization

INTRODUCTION

Since the pioneering work on poly(ethylene oxalate) by Carothers [1], the polymers of oxalic acid have been the subject of investigation of numerous groups. These studies have dealt mainly with either saturated aliphatic or aromatic polyoxalates. An article [2] as well as a patent [3] reported the study of preparation and decomposition of some unsaturated polyoxalates, but the polyesters appear not to have been characterized with respect to the molecular weight distribution, end group analysis, thermal stability, *etc.*

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*Corresponding author.

†Present address: Adhesive & Resin Dept., Iran polymer Institute, P.O. Box 14185-458, Tehran, Iran.

Polyoxalates derived from aliphatic diols are one of the members of the family of aliphatic polyesters which are recently used for the delivery of active agents (*i.e.*, pharmaceuticals, agrochemicals) in proper environment through biodegradation controlled release [4]. It was found that all aliphatic polyesters containing an aromatic structure or a double bond in the diacid component are not enzymatically degradable, while a double bond in the diol component, *e.g.*, 2-butene-1,4-diol, does not exclude the enzymatic cleavage [5, 6].

In addition, aliphatic polyesters are traditionally used in PVC plastisizers [7]. They may also be constructed as macroglycols or polyester polyols for preparation of block copolyesters [8] and polyester-based urethane elastomers [9]. Introduction of a carbon–carbon double bond in the diol component of polyester chains has been a core of our recent works [10–13].

The present study is concerned with a successful synthesis of poly(*cis*-2-butenylene oxalate) from diethyl oxalate and *cis*-2-butene-1,4-diol. The polyoxalates synthesis is, however, negatively affected by high tendency of the oxalate component to thermal degradation (decarboxylation) during the polymerization, and, in a lower extent, to forming some cyclic molecular species. Transesterification was used and optimized for the polyester synthesis. The polymer was characterized by means of elemental analysis, Fourier transform infrared (FTIR), ^{1}H-nuclear magnetic resonance (NMR), and Mass spectroscopy.

Gel permeation chromatography (GPC) was used for determination of molecular weight averages and distribution as well as detection of probable low oligomeric and cyclic molecules. Thermal behavior was studied by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA).

EXPERIMENTAL

Materials

Diethyl oxalate was prepared according to standard procedure [14], and its structure and purity was checked by the spectral data (NMR, IR) and by physical constants (boiling point, refractive index, and density). 2-Butene-1,4-diol (Aldrich, 99.5% *cis*) was used as received. Lead (II) oxide (Merck) was used without further purification.

Measurements

Elemental analysis was performed by a Heraeus CHNO Analyser system. The polymer solution viscosity was measured at 30°C in $CHCl_3$ using a Cannon-Fenske viscometer. FTIR spectra were measured by a Mattson 1000 spectrometer. ^1H-NMR spectra were obtained on an AC 80 Bruker using tetramethylsilane as an internal standard (solvent $CDCl_3$). GPC analysis was performed in tetrahydrofurane as solvent at 30°C with a Waters 150°C system equipped with Ultrastyragel columns (500, 10^3, 10^4, 10^5 Å), a data processing system, an RI detector, and a calibration curve for polystyrene standards.

Electron impact mass spectrum was obtained by a Finnigan MAT 8430 system. Thermal studies were performed by DSC/TG (STA-625 PL laboratories) and TGA (PL-1500 system) at a heating rate of 10°C/min. under N_2 atmosphere. X-ray diffraction (XRD) powder pattern was obtained *via* a philips PW 1840-90 system using Ni-filtered Cu-K_α radiation. The scan speed was 0.02 $2\theta/s$.

Polymer Synthesis

An ester-interchange (transesterification) polycondensation procedure was run for the polyester preparation. Thus, 10.2 g (0.10 mol) of diethyloxalate, 11.5 g (0.13 mol) of *cis*-2-butene-1,4-diol, 0.1 g of lead (II) oxide (PbO) as the catalyst and 0.1 g hydroquinone as the inhibitor were charged in a 200-mL four-necked reactor equipped with a silicon-sealed mechanical stirrer, heating mantle, thermometer, nitrogen inlet, and a reflux condenser. The mixture was heated at 120°C under a mild N_2 stream for 150 min. The apparatus arrangement was then changed into vacuum distillation, and the temperature was increased to 170°C for 30 min. under reduced pressure (150 mmHg) to remove ethanol and residual diol. The viscouse brown liquid was dissolved in hot chloroform, filtered, distilled the solvent from the filtrate, shaked vigorously with fresh methanol, and decantated. The last two steps were repeated several times, and finally methanol was completely removed by vaccum.

TABLE I Specifications of poly(*cis*-2-butenylene oxalate)

Property	*value*
Intrinsic viscosity[a], dL/g	0.29
Acid value[b], mg KOH/g polymer	57
Hydroxyl value[b], mg KOH/g polymer	130
Number average molecular weight[c], g/mol	600
Weight average molecular weight[c], g/mol	1320
Polydispersity index[c],	2.2
Degree of polymerization	4.2
Melting temperature[d], °C	85.36
Glass transition temperature[d]	No transition observed
Heat of fusion[d], cal/g	24.27
Entropy of fusion[d], cal/g°K	0.067
Initial decomposition temperature[e], °C	183
Degree of crystallinity[f], %	80

[a] In $CHCl_3$, 30 ± 0.1°C.
[b] From end-group chemical analysis through titration.
[c] From GPC, solvent THF, 30°C.
[d] From DSC/TG, under N_2, heating rate 10°C/min.
[e] From TGA-DTG, under N_2, heating rate 10°C/min.
[f] From wide-angle X-ray diffraction.

The yield was 60%. The specifications of the cream-colored solid product are given in Table I.

ANAL. Calcd. for ($C_6H_6O_4$): C 50.70%, H 4.23%, O 45.07%; Found C 50.75%, H 4.24%, O 45.01%.

The polymer was characterized by means of FTIR, ^{1}H-NMR (Fig. 1, Tab. II) and mass spectroscopy (Fig. 4), and by DSC/TG and TGA-DTG (Fig. 5, Tab. III) thermal techniques. XRD was used for the crystallinity study as well. The GPC chromatogram (Fig. 2) was also investigated.

RESULTS AND DISCUSSION

Synthesis and Chemical Characterization

Poly(*cis*-2-butenylene oxalate) was synthesized under optimized trans-esterification conditions, with diol excess of 30 mole percent, and by using of PbO as the catalyst, without an evidence of decarboxylation degradation which is a usual side reaction for the oxalic acid derivatives. We had earlier on failed to prepare the polymer *via* the direct poly-

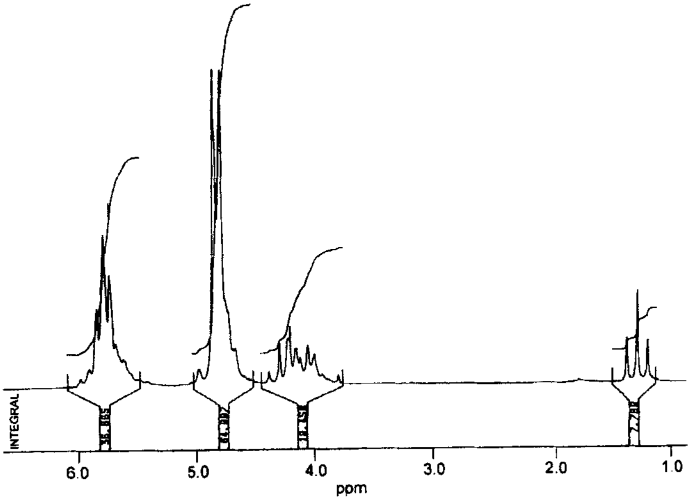
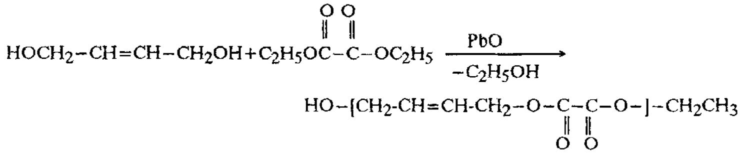


FIGURE 1 ^{1}H-NMR spectrum of poly(*cis*-2-butenylene oxalate).

TABLE II IR-Absorption band assignments for poly(*cis*-2-butenylene oxalate)

Wave number, cm^{-1}	*Relative intensity*	*Main assignments*
3438	Medium, Broad	O—H stretching
3030	Weak, Shoulder	=C—H stretching
2931, 2869	Medium, Medium	C—H stretching
1746	Strong	C=O stretching
1638	Medium	C=C stretching
1461	Medium	CH_2 bending (scissoring)
1315, 1169	Medium, Strong	C—O stretching
777	Weak	=C—H bending (out-of-plane)

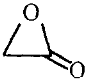
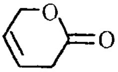
condensation [12].



$$HOCH_2{-}CH{=}CH{-}CH_2OH + C_2H_5O\overset{\overset{O}{\|}}{C}{-}\overset{\overset{O}{\|}}{C}{-}OC_2H_5 \xrightarrow[-C_2H_5OH]{PbO} HO{-}[CH_2{-}CH{=}CH{-}CH_2{-}O{-}\underset{\underset{O}{\|}}{C}{-}\underset{\underset{O}{\|}}{C}{-}O{-}]{-}CH_2CH_3$$

According to the different analytical data (Tab. I), the product is a highly crystalline low molecular weight polyester. The polyester was recognized to be a non-terminated polymer. In IR spectrum, OH stretching appears at 3438 cm^{-1}. Peaks of OCH_2CH_3 end groups in

TABLE III Fragments from mass spectroscopy of poly(*cis*-2-butenylene oxalate)

Fragment	*m/e*	*Relative intensity*
	40	66
$O{=}C{=}O$	44(base peak)	100
$H_2C{=}CH{-}CH{=}CH_2$	54	15
	58	42
$HO{-}CH{=}CH{-}CH{=}CH_2$	70	49
$CH_2{-}CH{=}CH{-}CH_2OH$	71	50
$CH_3CH_2O{-}C{\equiv}O$	73	43
$OCH_2CH{=}CHCH_2OH$	87	21
	97	22

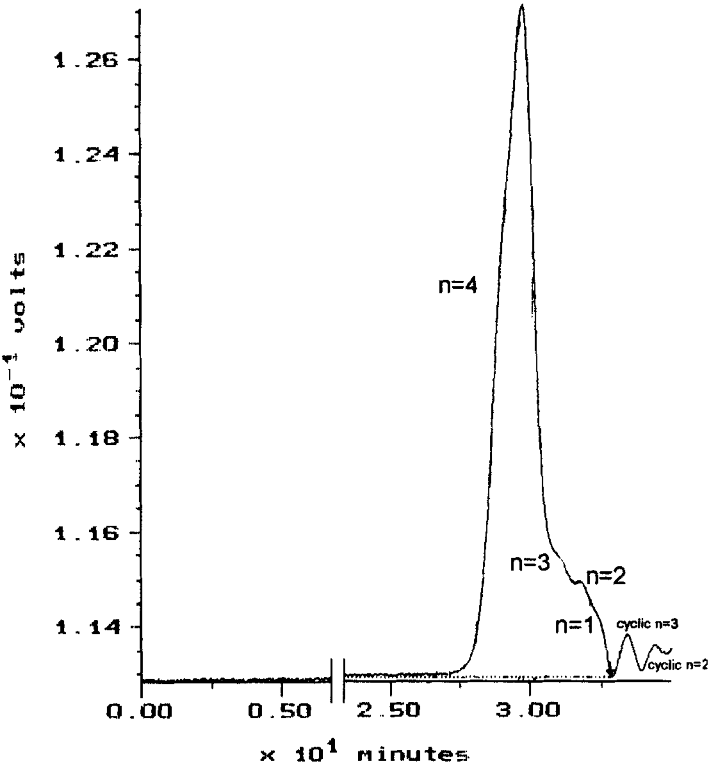


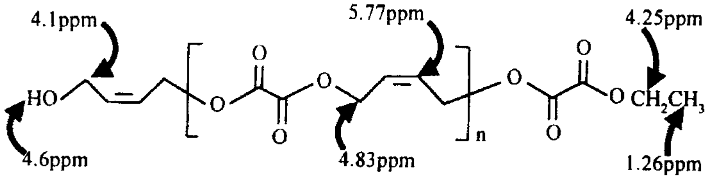
FIGURE 2 GPC chromatogram of poly(*cis*-2-butenylene oxalate); n = repeating unit.

NMR spectrum, appear at 4.2 ppm (CH_2, quartet) and 1.3 ppm (CH_3, triplet) (Fig. 1).

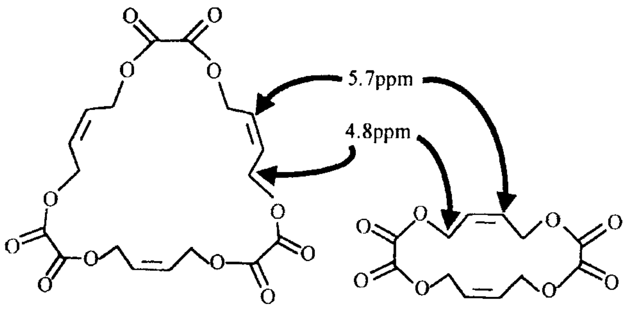
Peak of OH group (~4.65 ppm) [12] is hidden by the multiplet peaks of CH_2OOC which are overlapped by the quartet peak of OCH_2CH_3, and the all types of proton groups appear in the range of 3.9–4.9 ppm. Peaks at ~5.7 ppm are due to CH=CH. Other NMR chemical shift assignments are given in Figure 3.

Assignments of vibrational modes (IR) of the polyester is summarized in Table II. Figure 2 gives the GPC chromatogram of poly(*cis*-2-butenylene oxalate) before the last purification step (periods of shaking with methanol and decantating). Retention times for the macrocyclic species is higher than that for the linear chains. The most aboundent of the linear species corresponds to $n = 4$. The presence of the macrocycles is also confirmed by NMR spectrum. NMR chemical shift assignments are shown in Figure 3.

Mass spectral analysis of the polyester was also carried out (Fig. 4). Assignments [15] of the possible produced fragments (radical ions) and their relative intensities are tabulated in Table III. The proposed frag-



Linear non-terminated chain, n~4



Macrocycle n=3

Macrocycle n=2

FIGURE 3 ¹H-NMR chemical shift assignments for the linear and macrocyclic species (δ, ppm).

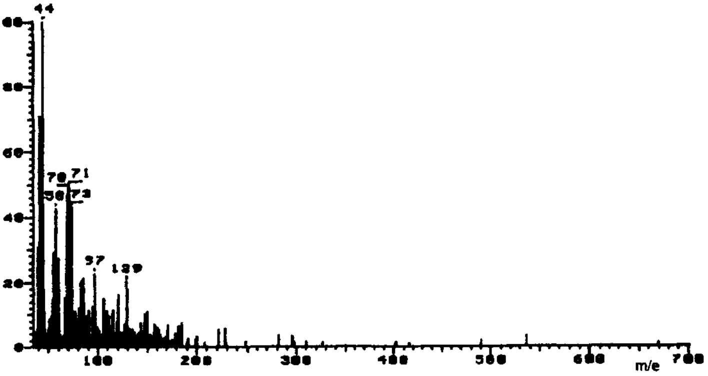


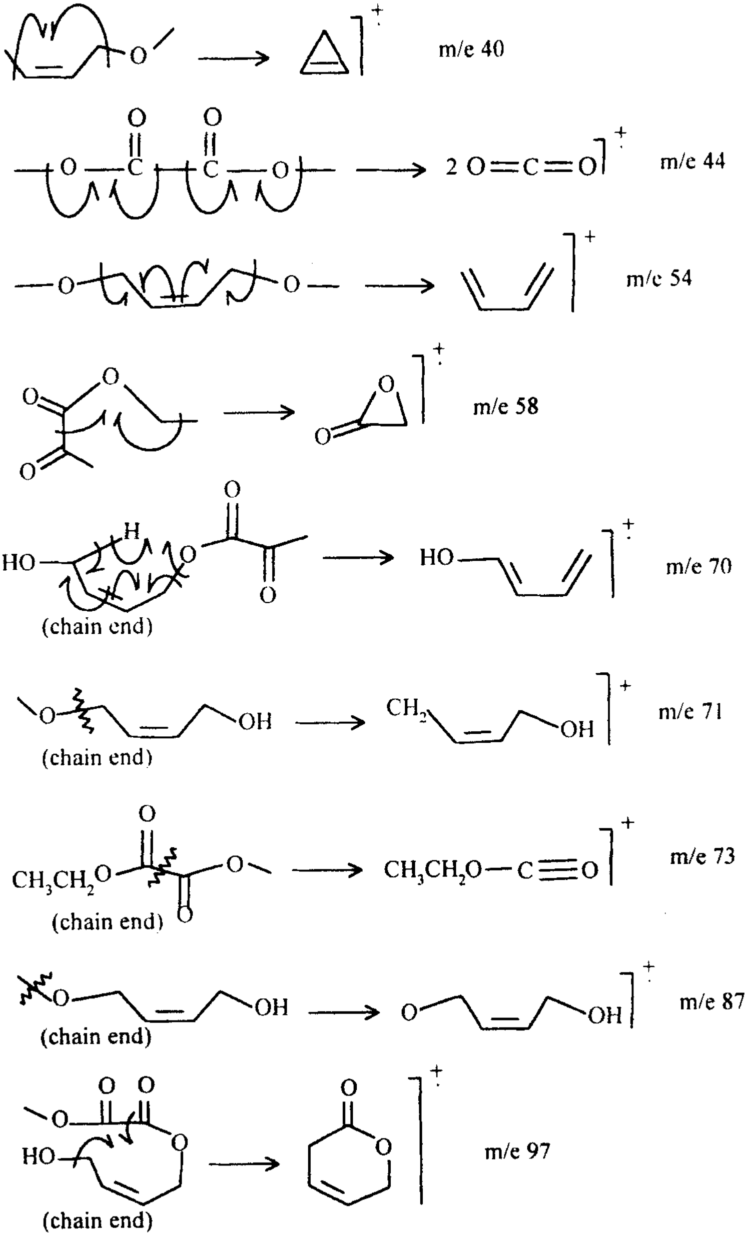
FIGURE 4 Mass spectrum of poly(*cis*-2-butenylene oxalate).

mentation mechanisms for producing of some of the mentioned radical ions are presented in Scheme 1. As we expected, degradation through decarboxylation which leads to evolution of CO_2, is the main type of fragmentation detected by the base peak at m/e 44. Cyclic species form the same fragments, except these fragments are produced at chain ends.

Thermal Characterization

Thermal behavior of poly(*cis*-2-butenylene oxalate) was studied and the thermograms of DSC/TG and TGA (as well as the derivative curve; DTG) are presented in Figure 5.

It was found the initial decomposition temperature (IDT, 183°C) is the lowest among the IDT of the other homologous polycarboxylates [11], but the temperature at 10% polymer weight loss (T_{10}) is the highest among them. A quantity named integral procedural decomposition temperature [16] (IPDT) as a means of summing up the whole shape of the normalized data curves, indicates that poly(*cis*-2-butenylene oxalate) is thermally more stable than its homologous polyesters. This is in agreement with its crystallinity and melting temperature which are the highest among the other members of the homologous series [10, 11]. DTG curve (Fig. 5b) which is the temperature corresponding to the maximum in the differential of the TGA curve, indicates a thermal decomposition temperature of 326°C, which is comparable with the exothermal peak at 320°C in the DSC thermogram (Fig. 5a).


m/e 40
2 O=C=O
m/e 44
m/e 54
m/e 58
HO
(chain end)
HO
m/e 70
OH
(chain end)
CH$_2$
OH
m/e 71
CH$_3$CH$_2$O
(chain end)
CH$_3$CH$_2$O—C≡O
m/e 73
OH
(chain end)
OH
m/e 87
HO
(chain end)
m/e 97

SCHEME 1

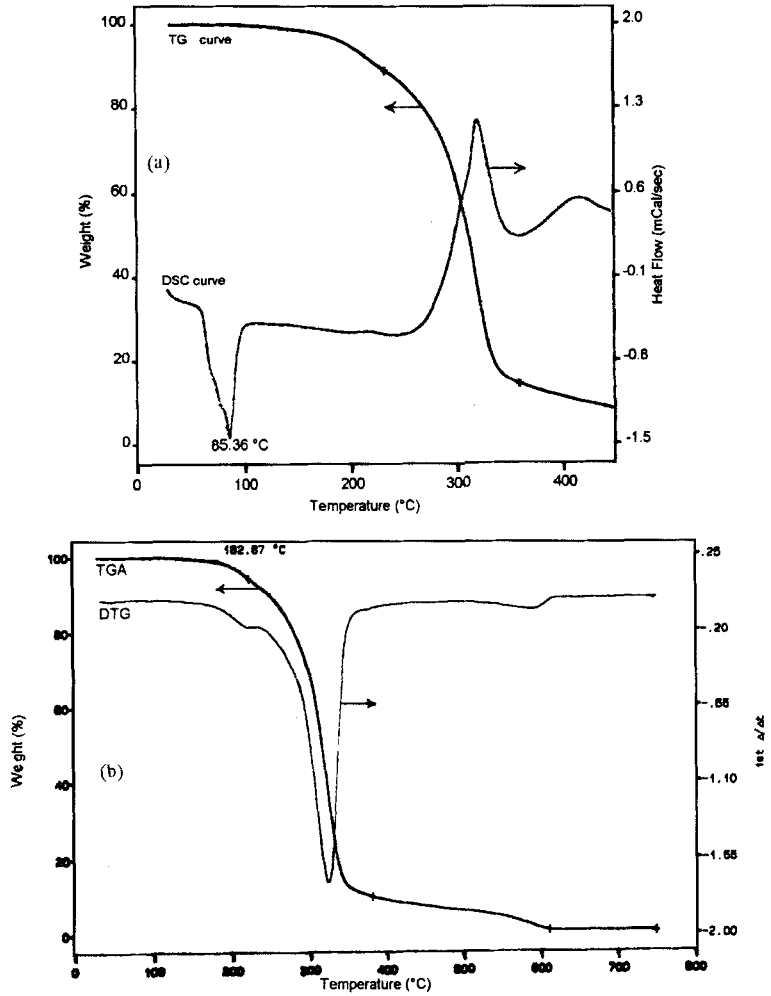


FIGURE 5 (a) DSC/TG, and (b) TGA-DTG thermograms of poly(*cis*-2-butenylene oxalate).

Two thermal regions are evident from the DSC diagram of the poly(*cis*-2-butenylene oxalate); melting transition (endothermal) at 85.36°C, and thermal decomposition (exothermal) at 320°C in DSC thermogram (Fig. 5a). So, there is no another exthothermal reaction such as crosslinking which had been detected by the DSC diagrams of other poly(*cis*-2-butenylene carboxylate)s [11].

Finally, the polyester thermally decomposes quite cleanly, leaving no substantial residue at 450°C (char yield ~7%wt).

CONCLUSIONS

Poly(*cis*-2-butenylene oxalate) is expected to have potential applications as enzymatically degradable and bio-compatible materials, and in block or segmented copolymers. The polyester was successfully synthesized through transesterification polycondensation without decarboxylation, and the produced non-terminated polyester was chemically and thermally characterized. Size-exclusion chromatography (GPC) showed low polydispersity (2.2) and formation of low amounts of macrocyclic species. The polyester is highly crystalline, and the overall thermal stability is higher than that of the other homologous polyesters.

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