Journal of Thermal Analysis, Vol. 38 (1992) 953-959

THE THERMAL DEGRADATION KINETICS OF POLY(DI-*n*-ALKYL ITACONATES)

I. G. Popovic, L. Katsikas and J. S. Velickovic

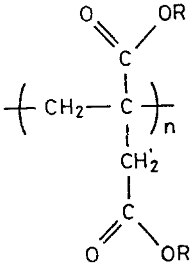
FACULTY OF TECHNOLOGY AND METALLURGY, BEOGRADE UNIVERSITY, KARNEGIJEVA 4,
P.O. BOX 494, YU-11001 BEOGRADE, YUGOSLAVIA

The non-oxidative thermal degradation kinetics of poly(di-n-alkyl itaconates), ranging from the methyl to the *n*-octyl derivatives, were studied by non-isothermal and isothermal TG. The thermal degradation activation energy and characteristic mass loss temperatures were found to decrease with increasing substituent size. The shapes of the DTG curves were dependent on the size of the alkyl substituent. The different DTG maxima were ascribed to various modes of initiation of depolymerisation. The thermal stability of poly(di-*n*-hexyl itaconate) was found to be independent of the initial molar mass of the sample in the range of $\overline{M}_w$ from 10^4 to 10^7 g/mol.

Keywords: kinetics, poly(di-*n*-alkyl itaconates), thermal stability

Introduction

Poly(di-*n*-alkyl itaconates) are vinylidene type polymers of the following structure:



This study deals with the non-oxidative thermal stability of poly(di–*n*–alkyl itaconates) with the *R* substituent ranging from the methyl to the *n*–octyl group. The influence of substituent length on the non-oxidative thermal degradation kinetics of poly(di-*n*-alkyl itaconates) will be discussed.

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Preliminary investigations of the thermal stability of poly(mono- and di-*n*-alkyl itaconates) were performed by Cowie and Haq [1]. Poly(dimethyl itaconate) (PDMI) was found to predominantly thermally degrade by depolymerisation [2]. Investigations of the thermal degradation mechanisms of other poly(di–*n*–alkyl itaconates) have shown that they are similar to that of PDMI [3]. The amount of monomer in the thermolysis volatiles does not depend on the size of the *n*–alkyl ester substituent and averages about 90%. Side chain scission, which, due to the structure of the side group, is more probable than in the case of poly(*n*–alkyl methacrylates), leads to the formation of small amounts of carbon dioxide, carbon monoxide and the corresponding 1–alkene, *n*–alkane, alcohol and acetate. A slight tendency towards crosslinking was registered in the higher poly(di–*n*–alkyl itaconates).

Experimental

Diethyl, di–*n*–butyl, di–*n*–hexyl and di–*n*–octyl itaconate were prepared by the standard esterification of itaconic acid (Aldrich, p.a.) with the corresponding alcohol (all Aldrich, p.a.). They were vacuum distilled before use. Dimethyl itaconate (Aldrich, p.a.) was recrystallised from methanol.

The polymers were obtained by polymerising the monomers in bulk in ampoules sealed under high vacuum. AIBN was used as the initiator. The polymerisations were taken to yields of not more than 20%. The molar masses of the polymers were determined by GPC (Knauer/Trilab) using poly(methyl methacrylate) samples (Röhm Gmbh, Germany) as standards. The polymerisation conditions and the weight average molar masses, $\overline{M}_w$, and the molar mass distributions, $\overline{M}_w/\overline{M}_n$, of the initial polymers are given in Table 1.

Table 1 Polymerisation conditions and molar masses of the initial poly(di–*n*–alkyl itaconates)

R	Designation	T_{pol} / °C	$\overline{M}_w$ / g·mol^{-1}	$\overline{M}_w/\overline{M}_n$
methyl	PDMI	35	$4.04 \cdot 10^5$	3.3
ethyl	PDEI	37	$2.93 \cdot 10^5$	2.5
n–butyl	PDBI	32.4	$8.01 \cdot 10^5$	2.8
n–hexyl	PDHI	31.8	$7.46 \cdot 10^5$	2.6
	PDHI–L	75	$3.47 \cdot 10^4$	2.4
	PDHI–H	31.8	$2.20 \cdot 10^7$	2.9
n–octyl	PDOI	50	$6.00 \cdot 10^5$	2.7

A Perkin Elmer TGS–2 instrument was used for the thermogravimetric measurements. Non-isothermal experiments were performed in the temperature range 30° to 500°C at heating rates of 0.625, 2.5, 10, 20 and 40 deg/min. Isothermal experiments were done in the range 240° to 310° at 10°C intervals. The average sample size was 5 mg and the nitrogen flow rate 25 cm^3/min. The non-isothermal TG data were analysed by the Flynn-Wall method [4], while the differential method [5, 6] was used for the isothermal data.

Results and discussion

A typical set of non-isothermal TG curves of a poly(di-*n*-alkyl itaconate) is shown in Fig. 1. The temperatures of 10% mass loss of the polymers, $T_{10\%}$, derived from the non-isothermal TG-curves obtained at 25 deg/min, given in Table 2, decrease with increasing length of the substituent. Only the value of $T_{10\%}$ of poly(di–*n*–octyl itaconate) (PDOI) is somewhat higher than the corresponding value of poly(di–*n*–hexyl itaconate) (PDHI). This increase is a consequence of the crosslinking occurring during the thermolysis of this polymer [3]. These results are in agreement with the trend found in the structurally similar poly(*n*–alkyl methacrylates) [7]. However, no crosslinking has been reported during the thermolysis of poly(*n*-alkyl methacrylates). In all cases the carbon residues at 500°C were found to be 2–3%.

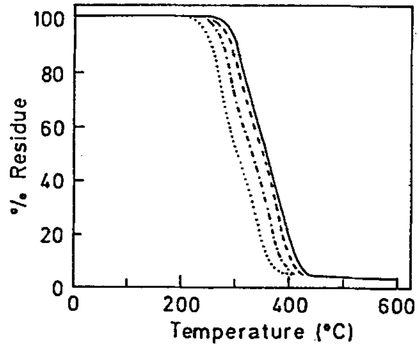

Fig. 1 Non-isothermal TG curves of PDHI, heating rates (· · · · ·) 2.5, (— · — · —) 10, (— — —) 20 and (———) 40 deg/min, nitrogen flow rate 25 cm^3/min

The rate constants of isothermal mass loss of PDMI, poly(di-*n*-butyl itaconate) (PDBI) and PDHI, *k* were determined by the differential method, as defined by Letort [5], and are given in Table 3. The values of *k* increase significantly with increasing alkyl substituent size at the same degradation temperature. Although it has been established that the apparent reaction order, *n*, does not have any physical meaning when applied to such complex reaction mechanisms as polymer degradation, it was determined that n, considered as a relative parameter, increases with substituent size. For example, the values of n at 300°C, determined by the differential method, are 2.1, 3.0 and 5.4 for PDMI, PDBI and PDHI, respectively.

Table 2 Characteristic mass loss temperatures, heating rate 2.5 deg/min, nitrogen flow rate 25 cm^3/min

Polymer	$T_{10\%}$ /°C	$T_{50\%}$ /°C	$T_{90\%}$ /°C
PDMI	272	292	330
PDEI	261	287	343
PDBI	248	277	321
PDHI	242	285	335
PDOI	256	305	355

Table 3 The rate constants of isothermal mass loss of PDMI, PDBI and PDHI determined by the differential method

Temperature / °C	$k_{PDMI}\times10^4$ / s^{-1}	$k_{PDBI}\times10^4$ / s^{-1}	$k_{PDHI}\times10^4$ / s^{-1}
240	–	–	1.8
250	–	2.6	4.5
260	–	4.3	77
270	–	7.0	96
280	–	11.1	273
290	–	17.3	247
300	5.1	26.7	268
310	10.8	40.5	247
320	30.3	–	–
330	36.3	–	–
340	33.5	–	–
350	45.2	–	–

The values of overall thermal degradation energy, E_a , determined from both non-isothermal and isothermal TG data, are given in Table 4. Comparison of the E_a's obtained from both types of TG measurements indicates that the values are the same within experimental error. The values of the E_a 's decrease with increasing substituent size. The Arrhenius pre-exponential factors are of the same order of magnitude, within experimental error, regardless of substituent size (Table 4).

The thermal stability of poly(di-*n*-alkyl itaconates) was found not to depend on the molar mass of the polymers. A series of PDHI samples ranging in $\bar{M}_w$, from 10^4 to 10^7 g/mol were subjected to non-isothermal TG. The characteristic mass loss temperatures, temperatures of the DTG maxima, as well as the E_a's, did not change with polymer molar mass (Table 5).

Table 4 The dependence of E_a on the size of the ester substituent

Polymer	E_a / kJ·mol^{-1} (Flynn–Wall)	E_a / kJ·mol^{-1} (differential)	A / s^{-1}
PDMI	124± 9	124±6	(1.5±0.1)·10^8
PDEI	124±15	–	–
PDBI	121±12	116±2	(1.0±0.1)·10^8
PDHI	118±14	115±6	(8.0±0.4)·10^8
PDOI	103±14	–	–

Table 5 The dependence of PDHI thermal stability on the initial molar mass of the sample

$\bar{M}_w$ / g·mol^{-1}	$T_{10\%}$ / °C	E_a / kJ·mol^{-1}	$T_{DTGmax1}$ / °C	$T_{DTGmax2}$ / °C
3.5·10^4	241	116±14	268	298
3.7·10^5	239	118±14	267	320
2.2·10^7	242	115±12	271	320

The shapes of the DTG curves of the investigated poly(di-*n*-alkyl itaconates) are shown in Fig. 2 and the temperatures of the DTG maxima in Table 6. The methyl and ethyl derivatives are characterised by a single peak with a shoulder which becomes a plateau in the case of PDBI. Two distinct peaks are registered in the case of the hexyl and octyl derivatives. The size of the first DTG peak decreases with increasing alkyl chain length. The position of the saddle between the two DTG maxima is not dependent on the size of the ester substituent. When a heating rate of 0.625 deg/min was applied, in all cases the saddle was registered at about 290°C (Fig. 2).

As it has been established that the major thermolysis reaction of poly(di-*n*-alkyl itaconates) is depolymerisation [1–3], the two DTG maxima can most probably be ascribed to different depolymerisation initiation modes, as is the case in the thermal degradation of poly(methyl methacrylate) [8]. The first DTG maximum would correspond to end chain initiation, while the second could be assigned to the main chain initiation of depolymerisation. Side chain scission, which leads to main chain scission thus initiating depolymerisation, probably takes place to a minor extent in the whole temperature range of mass loss. This conclusion is supported by the fact that the susceptibility of poly(di-*n*-alkyl itaconates) to side chain scission does not depend on alkyl substituent length [3].

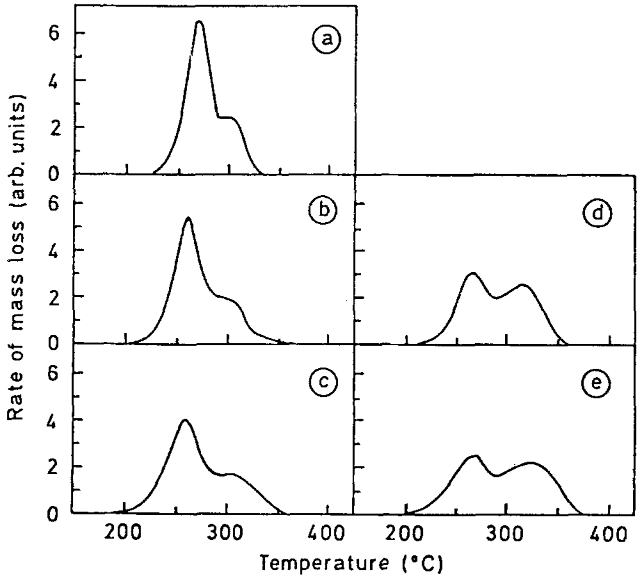

Fig. 2 DTG curves of a) PDMI, b)PDEI, c)PDBI, d) PDHI and PDOI, heating rate 2.5 deg/min, nitrogen flow rate 25 cm^3/min

Table 6 The DTG maxima of the investigated poly(di-*n*-alkyl itaconates), heating rate 0.625 deg/min, nitrogen flow rate 25 cm^3/min

Polymer	$T_{DTGmax1}$ / °C	$T_{DTGmax2}$ / °C
PDMI	268	300*
PDEI	258	295**
PDBI	260	300
PDHI	263	318
PDOI	269	323

*position of shoulder
**middle of plateau

The first DTG peak of the lower poly(di-*n*-alkyl itaconates) is larger than the second implying the existence of considerable chain end unsaturation in these polymers. In other words, the double bonds at the chain ends do not originate only from termination by disproportionation in radical polymerisation. Nagai and Yoshida [9] have proposed that, due to the allylic structure of di-itaconate monomers, chain transfer to monomer is favoured during free radical polymerisation. Such a reaction could be an additional source of chain end unsaturation. This possibility will be discussed in greater detail in a future publication.

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Zusammenfassung — Mittels nichtisothermer und auch isothermer TG wurde die nichtoxidative thermische Zersetzungskinetik von Poly(di-*n*-alkylitakonaten) untersucht, dabei bewegt sich die Länge der Alkylkette von Methyl bis *n*-Oktyl. Die Aktivierungsenergie der thermischen Zersetzung und die charakteristischen Masseverlusttemperaturen nehmen mit steigender Substituentlänge ab. Aussehen der DTG-Kurven hängt von der Größe der Alkylkette ab. Die verschiedenen DTG-Maxima wurden verschiedenen Initiierungs schritten der Depolymerisierung zugeschrieben. Man fand, daß im Intervall M_w zwischen 10^4 und 10^7 g·mol die thermische Stabilität der Poly(di-*n*-hexylitakonate) unabhängig von der anfänglichen molaren Masse der Probe ist.