

The thermal stability of some poly(di-aryl itaconates)

I. G. Popović*, V. Galogaža, L. Katsikas, and J. Veličković

Faculty of Technology and Metallurgy, Karnegijeva 4, P.O. Box 494, YU-11001 Belgrade, Yugoslavia

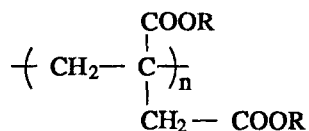
Summary

The non-oxidative thermal stability of poly(di-aryl itaconates) was established by thermogravimetric analysis. The polymers investigated were poly(diphenyl itaconate) (PDPHI), poly(di-ortho-, meta- and para-tolyl itaconates) (PDoTI, PDmTI, PDpTI) and poly(dibenzyl itaconate) (PDBzI). The shapes of the DTG curves indicated that at least two reactions were involved in the degradation mechanisms. Carbonaceous residues were registered in all polymers. Preliminary thermal degradation experiments showed that the polymers decomposed mainly by depolymerisation with side chain scission registered in the cases of PDoTI and PDBzI. All polymers except PDBzI crosslinked slightly at lower degradation temperatures.

Introduction

Generally, polymers of aromatically substituted vinylidene compounds have not been extensively investigated. The synthesis and properties of poly(diphenyl itaconate) and poly(ditolyl itaconates) have been studied by Veličković and Cowie and their coworkers (1,2,3). However, little is known about the thermal stability of these polymers. The goal of this study was to initially assess the thermal degradation kinetics and mechanisms of these polymers in the absence of oxygen.

The polymeric esters of itaconic acid, i.e. 1-propene-2,3-dicarboxylic acid have the following structure



where R can be an alkyl or aryl substituent.

Studies of the thermal stability of poly(di-n-alkyl itaconates) (4,5) have shown that the major thermal degradation pathway of these polymers is depolymerisation, i.e. formation of the monomer. Other organic compounds as well as carbon monoxide and carbon dioxide, which are formed as a

*To whom offprint requests should be sent

consequence of reactions in the side chains, are present in small amounts. At lower degradation temperatures, at which no polymer mass loss is detectable (about 200°C), crosslinking occurs to a small extent. However, this reaction becomes negligible upon the initiation of depolymerisation. So far no data on the thermal degradation of poly(di-aryl itaconates) have been found in the literature.

In order to analyse the effects of the presence and positions of various aromatic ester substituents, the thermal stability of the following polymers was studied: poly(diphenyl itaconate) (PDPhI), poly(di-ortho-, meta- and para-tolyl itaconates) (PDoTI, PDmTI and PDpTI) and poly(dibenzyl itaconate) (PDBzI).

Experimental

Monomer and polymer synthesis

Diphenyl itaconate and di-ortho-, meta- and para-tolyl itaconates were prepared by esterifying itaconic acid (Merck, p.a.) with the corresponding phenol (all Merck, p.a.) in the presence of phosphorous pentoxide (Merck, p.a.) according to the procedure presented in ref. (1). Dibenzyl itaconate was synthesized by esterifying itaconic acid (Merck, p.a.) with benzyl alcohol (Merck, p.a.). The polymerisations were performed in bulk or benzene solution at various temperatures using different α,α' -azobisisobutyronitrile concentrations. The polymers were purified by multiple dissolution/precipitation in benzene/methanol. The molar masses of the unfractionated polymers ranged from 5×10^4 to 5×10^5 g/mol and were obtained from limiting viscosity number measurements (2). In some cases the molar masses and molar mass distributions were determined by gel permeation chromatography (GPC) (Knauer-Trilab) using a poly(methyl methacrylate) calibration.

Thermogravimetric analysis

A Perkin Elmer TGS-2 instrument was used for thermogravimetric measurements. Non-isothermal experiments were performed in the temperature range 30° to 500°C at heating rates of 2.5, 10, 20 and 40°/min. Isothermal runs were done in the range 280° to 410°C with an initial heating rate to the desired temperature of 160°/min. The average sample size was 6 to 8 mg and the nitrogen flowrate 25 cm³/min.

The non-isothermal data were analysed by the Flynn-Wall method (6). This is a fast and simple method which enables the determination of thermal degradation activation energies on the basis of three or more thermogravimetric runs performed at different heating rates. The isothermal data were analysed by the differential method.

Thermal degradation experiments

The polymers were degraded in a small 250W furnace at 250°, 280° and 300°C. The samples were degassed (ca 10⁻⁵ mbar) before heating. The average sample size was about 100 mg. The molar mass of the polymer residues was determined by GPC. The volatile degradation products were analysed by gas chromatography using a Perkin Elmer 8500 instrument provided with a capillary column and FID detector. A more detailed description of the analytical techniques used may be found in ref. (7).

Results and Discussion

Typical non-isothermal thermogravimetric curves of poly(di-aryl itaconates) are shown in Figure 1. The slopes of the obtained curves vary and these differences can be clearly distinguished in the differential thermogravimetric (DTG) curves, Figure 2.

The shapes of the DTG curves of PDPPhI, PDmTI and PDpTI are very similar and have two maxima. The DTG curve of PDoTI also has two maxima, however, the first peak is considerably smaller than the second. The shapes of these curves indicate that at least two reactions are involved in the thermal degradation of these polymers.

The shape of the PDBzI DTG curve differs to the others and consists of a plateau followed by a peak. This polymer, although containing an aromatic substituent, should be regarded separately because the methylene group inserted between the carboxylic and phenyl group affects the behaviour of the polymer.

Characteristic mass loss temperatures of the polymers, recorded from the data of Figure 1, are presented in Table 1, while the temperatures of the DTG maxima are given in Table 2. Comparison of the temperatures at which

Table 1. Characteristic mass loss temperatures ($^{\circ}\text{C}$) of some poly(di-aryl itaconates), heating rate $2.5^{\circ}/\text{min}$, nitrogen flowrate $25\text{ cm}^3/\text{min}$

Mass loss (%)	PDPPhI	PDoTI	PDmTI	PDpTI	PDBzI
5	279	276	274	275	211
50	332	336	341	335	322

Table 2. DTG maxima of some poly(di-aryl itaconates), heating rate $2.5^{\circ}/\text{min}$, nitrogen flowrate $25\text{ cm}^3/\text{min}$

Polymer	T_{DTGmax1} ($^{\circ}\text{C}$)	T_{DTGmax2} ($^{\circ}\text{C}$)	ΔT ($^{\circ}\text{C}$)
PDPPhI	306	356	50
PDoTI	298	354	56
PDmTI	302	353	51
PDpTI	297	349	52
PDBzI	plateau at about 265	329	-

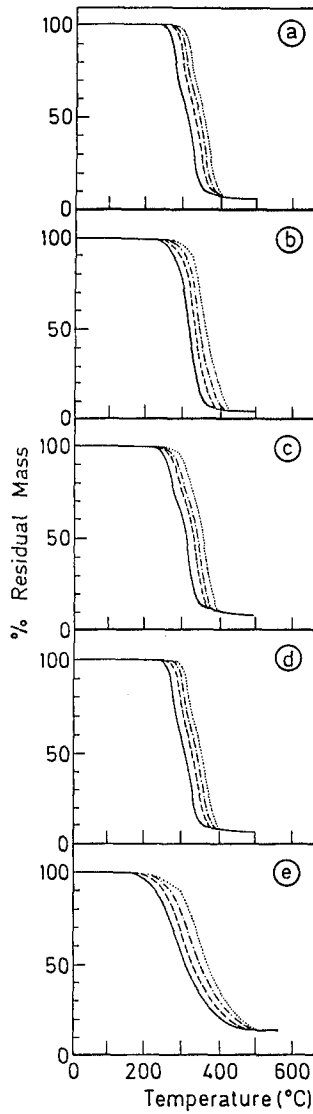


Fig. 1

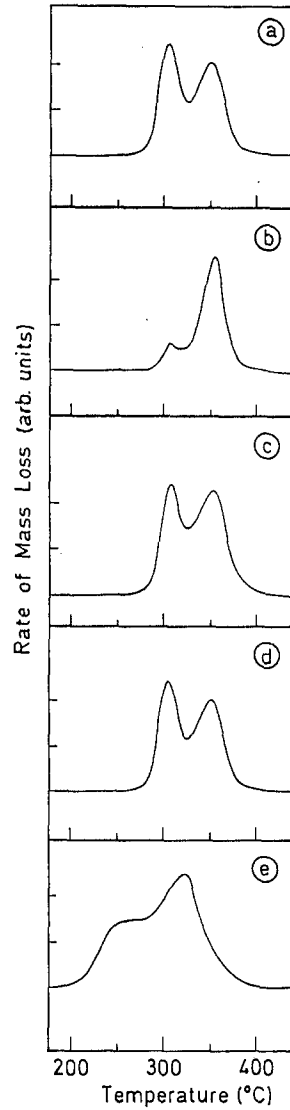


Fig. 2

Figure 1. Non-isothermal thermogravimetric curves of a) PDPbI (sample I), b) PDoTI (sample II), c) PDMTI (sample I), d) PDpTI (sample I) and e) PDBzI (sample I), heating rates (—) 2.5, (-----) 10, (- - -) 20 and (.....) 40°/min, nitrogen flowrate 25 cm³/min

Figure 2. Non-isothermal DTG curves of a) PDPbI, b) PDoTI, c) PDMTI, d) PDpTI and e) PDBzI (samples same as in Fig. 1), heating rate 2.5°/min, nitrogen flowrate 25 cm³/min

Table 3. DTG maxima of PDPPhI obtained at various heating rates, nitrogen flowrate 25 cm³/min

Heating Rate	T _{DTGmax1} (°C)	T _{DTGmax2} (°C)	DT (°C)
1.25	290	339	49
2.5	306	356	50
5	315	370	55
10	328	383	55
20	344	398	54
40	365	420	55

5% mass loss is attained, T_{5%}, indicates that this temperature is approximately the same for phenyl and tolyl derivatives, about 275°C. The value for the benzyl derivative is somewhat lower, about 210°C.

It is interesting to notice that the temperature differences of the DTG maxima ΔT , of PDPPhI, PDMTI and PDPtI are approximately the same and are not influenced by the heating rate (example of PDPPhI shown in Table 3). When PDoTI is heated at a higher heating rate, only one broad DTG peak, with a maximum corresponding to the second peak of the other polymers, is registered. The DTG maximum of PDBzI lies between the maxima of the other polymers.

A carbonaceous residue at 500°C was registered in all the investigated polymers. The amounts of this residue, shown in Table 4, vary from 5 to 15% for PDoTI and PDBzI, respectively.

The isothermal thermogravimetric curves for the various polymers are similar and typical runs are shown in Figure 3.

The overall thermal degradation activation energies, E_a's, calculated from both non-isothermal and isothermal data, are presented in Table 5. The E_a's of different samples of the same polymer in most cases vary somewhat even when the same calculation method is used. These differences could be caused by varying molar masses and/or molar mass distributions of the samples.

The free radical polymerisation of diphenyl- and ditolyl itaconates is generally slow due to high steric hindrances in the monomer molecules. At

Table 4. Amounts of carbonaceous residue registered at 500°C by non-isothermal TGA, nitrogen flowrate 25 cm³/min

Polymer	PDPPhI	PDoTI	PDMTI	PDPtI	PDBzI
Amount of Residue (%)	8	5	7	10	15

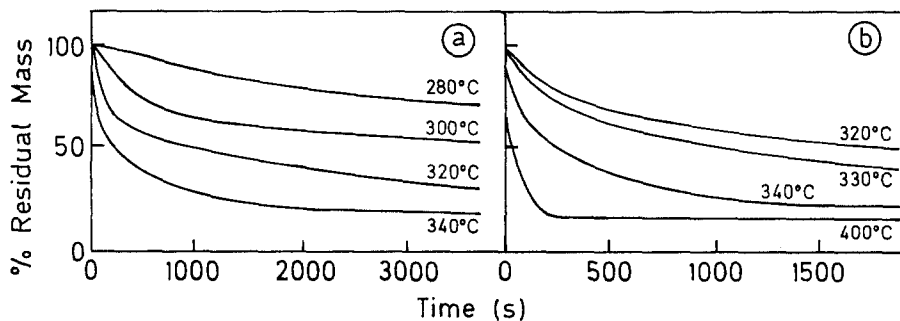


Figure 3. Typical isothermal thermogravimetric runs of poly(di-aryl itaconates), heating rate to set temperature $160^{\circ}\text{C}/\text{min}$, nitrogen flowrate $25\text{ cm}^3/\text{min}$, a) PDPHl (sample I), b) PDBzI (sample I)

low conversion the polymer molar masses are low, especially in the case of PDoTI, whereas when the polymerisations are taken to higher yields, branching and crosslinking occur. GPC chromatograms of some of the PDPHl and PDTI samples indicated that the molar mass distributions were bimodal, i.e. that small fractions of very high molar mass polymer were present in the samples.

It was, therefore, difficult to draw definite conclusions about the influence of ester substituents on the activation energy. The average E_a for all the polymers ranged from 140 to 150 kJ/mol, which is slightly higher than those determined for poly(di-n-alkyl itaconates) (100 to 130 kJ/mol) (4,5). In the case of the phenyl and tolyl derivatives, two ranges of E_a 's,

Table 5. Thermal degradation activation energies of some poly(di-aryl itaconates) expressed in kJ/mol

Method	Flynn - Wall			Differential		
	Mass loss Range (%)	Sample I	Sample II	Temp. Range ($^{\circ}\text{C}$)	Sample I	Sample II
PDPHl	0 - 40 50 - 80	120 154	146 154	280 - 330	118	145
PDoTI	0 - 10 20 - 90	93 128	113 140	280 - 330	121	146
PDmTI	0 - 30 40 - 80	106 132	138 162	280 - 330	122	140
PDpTI	0 - 40 50 - 80	124 144	127 144	280 - 330	154	167
PDBzI	10 - 70	146	-	320 - 410	158	-

differing on the average by 25 kJ/mol, were registered (see Table 5). The E_a of PDBzI was uniform throughout the mass loss range.

Preliminary thermal degradation experiments at 250° to 300°C indicated that the main thermolysis products of PDPhI, PDmTI and PDpTI were the corresponding monomers. In the cases of PDoTI and PDBzI, side chain scission leading to the formation of the corresponding volatile product, o-cresol or benzyl alcohol, respectively, was as prevalent as depolymerisation.

Upon degradation at 250°C, the residues of the phenyl and tolyl derivatives were partly insoluble. The molar masses of the soluble fractions of polymer residues were lower than those of the initial polymers. No insoluble material was detected in these polymers after degradation at 300°C.

In the case of PDBzI no crosslinking was registered. Analysis of the thermolysis volatiles and residues indicates that thermal degradation proceeds via depolymerisation, main chain scission and side chain scission.

As previously demonstrated in the thermal degradation of poly(methyl methacrylate) (8), the shapes of the DTG curves of polymers that thermally degrade predominantly by depolymerisation can be related to the modes of initiating this reaction. The first DTG peak is ascribed to chain end initiation and the second to random main chain scission initiation of depolymerisation.

As GC analysis has shown that the monomer is the major product evolved in the thermolysis of PDPhI, PDmTI and PDpTI, the DTG curves of these polymers could also be analysed in this way. The DTG curve of PDoTI slightly varies from the general shape of these curves (see Figure 2). The cause of this different behaviour has not yet been established. It is possible that during the polymerisation of di-ortho-tolyl itaconate, chain transfer processes are favoured leading to low polymer molar masses and fewer chain end double bonds formed by disproportionation. The decreased number of these double bonds would give rise to a smaller first DTG peak related to the chain end initiation of depolymerisation. At higher degradation temperatures, side chain scission becomes a major reaction, as evidenced by the substantial amount of o-cresol in the thermolysis products. The formed lateral macroradical can then easily rearrange leading to main chain scission and subsequent depolymerisation. This affinity to side chain scission may be due to PDoTI having ester substituents that are the most sterically hindered of the tolyl isomers.

Conclusions

Preliminary investigations of the thermal stability of poly(di-aryl itaconates) indicate that they are more stable than their n-alkyl counterparts. PDPhI, PDmTI and PDpTI degrade predominantly by depolymerisation, while side chain scission also occurs in the cases of PDoTI and PDBzI. At lower degradation temperatures, the phenyl and tolyl derivatives tend to crosslink slightly. The tendency of these polymers to branch and crosslink already during polymerisation needs to be further elucidated before detailed analysis of the thermal degradation mechanisms can be performed.

Acknowledgements

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