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THE THERMAL DEGRADATION KINETICS OF ISOMERIC POLY(DIPROPYL ITACONATES)

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Abstract

Non-isothermal thermogravimetry was performed in a dynamic nitrogen atmosphere, on a series of poly(di-*n*-propyl itaconates) (PDnPI) and poly(di-*iso*-propyl itaconates) (PDiPI) which had been prepared in the presence of various amounts of the chain transfer agent *n*-dodecyl mercaptan (DDM).

Differential thermogravimetry (DTG) showed that both polymers degraded in two stages. The DTG curve of PDnP1 had a large first peak followed by a smaller shoulder, whereas the DTG curve of PDiPI was composed of two peaks of almost equal heights. The addition of DDM during the polymerisations in both cases resulted in a similar decrease in the relative area of the first peak.

Keywords: kinetics, poly(di-propyl itaconates), polymer structure, thermal degradation

Introduction

Itaconic acid, methylene succinic acid, is an interesting starting material for a wide variety of polymeric materials as, not only is the parent substance available from non-petrochemical sources [1], but also, being a dibasic acid, the properties of the polymers can be tailored by simply changing the nature of the ester substituents [2]. Thus, a variety of di-, mono- and mixed esters of itaconic acid have been prepared most of which can be polymerised to relatively high molar mass polymers [3–5].

Although the solution [6–8] and solid state properties [2, 9–12] of these polymers have been extensively studied, their thermal degradation has been a neglected field of research. After a preliminary paper [13] dealing with the thermal degradation of di- and mono-*n*-alkyl esters of poly(itaconic acid), in which it was established that depolymerisation was the major degradation route in the case of poly(di-*n*-alkyl itaconates), only recently have the detailed degradation kinetics [14] and mechanism [15, 16] of these polymers been established. In these papers the similarities and differences to the structurally similar poly(*n*-alkyl methacrylates) were discussed in detail.

Research on the thermal degradation of branched dialkyl esters of poly(itaconic acid) has started only very recently [17, 18]. In this work it was established that, as

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is the case during the thermal degradation of the corresponding esters of the structurally similar poly(methacrylic acid), ester decomposition reactions are of increased importance in the case of poly(di-*iso*-propyl-) (PDiPI) and poly(di-*sec*-butyl itaconate) (PDsBI) when compared to poly(di-*n*-propyl-) (PDnPI) and poly(di-*n*-butyl itaconate) (PDnBI). However, depolymerisation remains a significant degradation route.

In this paper, the consequences of the effects of altering the polymerisation conditions on the thermal degradation kinetics of PDnPI and PDiPI will be presented and discussed.

Experimental

Di-*n*-propyl- (DnPI) and di-*iso*-propyl itaconates (DiPI) were prepared by the standard acid-catalysed esterification of itaconic acid with 1-propanol and 2-propanol, respectively. A Dean-Stark apparatus was used to remove the water formed during the course of the reaction. After the usual work up procedures, washing first with 10% NaOH then with water to neutral and drying over anhydrous calcium chloride, the benzene employed as solvent in the esterification was removed under reduced pressure before the crude diesters were distilled under high vacuum.

For the polymerisations, monomer solutions containing 0.5 mol% α,α'-azobisisobutyronitrile (AIBN) in either DnPI or DiPI were prepared. The solutions were charged in 10 g portions into glass ampoules. The ampoules were purged with nitrogen for 30 min and the required amounts of *n*-dodecyl mercaptan (DDM) added from a Hamilton microlitre syringe. The ampoules were then sealed under

Table 1 Polymerisation conditions for the preparation of PDnPI and PDiPI. Polymerisation temperature 60°C, AIBN concentration 0.5 mol%

Monomer	Polymer	Mass monomer/ g	Vol DDM/ μL	Polym. time/ min	Conversion/ % h^{-1}
DnPI	N–1	13.5594	0	60	2.6
DnPI	N–2	10.3183	5	60	2.6
DnPI	N–3	10.7363	10	60	2.5
DnPI	N–4	10.4953	25	60	2.2
DnPI	N–5	10.6168	50	60	1.7
DnPI	N–6	10.1015	100	60	0.8
DiPI	I–1	11.4158	0	60	2.7
DiPI	I–2	10.0971	5	60	2.9
DiPI	I–3	10.1204	10	60	2.3
DiPI	I–4	9.9682	25	60	2.3
DiPI	I–5	10.0693	50	75	1.6
DiPI	I–6	10.4203	100	90	1.1

high vacuum and placed for 60 min in an oven thermostatted at 60°C. Details of the polymerisation conditions are given in Table 1.

The polymer formed was recovered by precipitation with methanol containing 5 vol% water. Purification of the polymers was performed by reprecipitation from benzene solutions using methanol containing 5 vol% water as the precipitant. The polymers were dried to constant mass under vacuum at room temperature.

Non-isothermal thermogravimetry (TG) and differential thermogravimetry (DTG) were performed under a dynamic nitrogen atmosphere (20 cm^3 min^{-1}) at heating rates of 2.5, 10, 20 and 40°C min^{-1} using a Perkirt Elmer TGS-2 apparatus equipped with a first derivative computer (FDC) accessory for the simultaneous recording of TG and DTG curves. The sample masses ranged between 2 and 3 mg.

Apparent thermal degradation activation energies, E_a, were determined from the TG curves using the Flynn-Wall method [19]. The DTG curves were digitised in 5°C steps and deconvoluted into the two constituent peaks using a non-commercial peak deconvolution program.

Results and discussion

The polymerisation conversions, as can be seen from Table 1, were kept sufficiently low to ensure that the added chain transfer agent (DDM) was not significantly depleted during the course of the reaction. Chain transfer to DDM was degenerative in the case of both monomers as indicated by the decreasing polymer yield with increasing DDM concentration.

The non-isothermal TG curves, recorded at heating rates of 2.5, 10, 20 and 40°C min^{-1}, for all the prepared polymers ran parallel to one another indicating that the heating rate did not change the thermal degradation mechanism. Typical examples of the TG curves for both polymers, prepared in the absence of DDM, are given in Figs 1 a and b for PDnPI and PDiPI, respectively.

The obvious difference that can be seen between the two sets of TG curves is the amount of residue at 600°C. The residue amounts to about 10% in the case of PDiPI, but only about 1% for PDnPI. The sets of TG curves obtained for the polymers prepared in the presence of DDM were very similar.

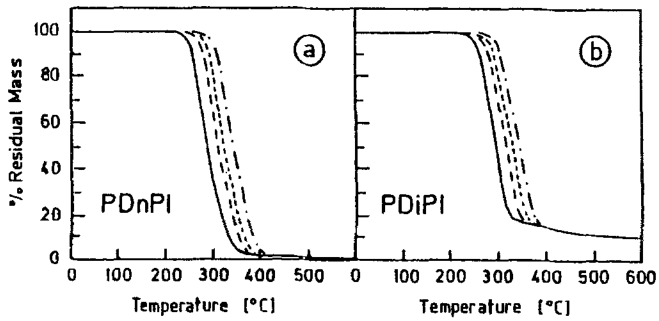

Fig. 1 Non-oxidative TG curves for (a) PDnPI and (b) PDiPI obtained at the heating rates (—) 2.5, (– –) 10, (------) 20 and (– · –) 40°C min^{-1}. Sample mass 2– 3 mg. Nitrogen flow rate 20 cm^3 min^{-1}

The mass loss temperatures corresponding to 10, 50 and 90% mass loss, $T_{5\%}$ $T_{50\%}$ and $T_{90\%}$ respectively, are given in Table 2 for all the polymers studied. It can be seen that the mass loss temperatures for the PDiPI series are slightly higher than those for the PDnPI series. Also the mass loss temperatures for both series of polymers tend to increase with increasing amount of DDM. An explanation for this can be seen when the TG curves, obtained at a heating rate of 10°C min^{-1}, for the polymers prepared in the absence of DDM are compared with those for the polymers prepared in the presence of 100 μL DDM. See Figs 2 a and b for PDnPI and PDiPI, respectively.

The apparent thermal degradation activation energies, E_a, for all the polymers studied were calculated using the Flynn-Wall method [19]. The values for all the

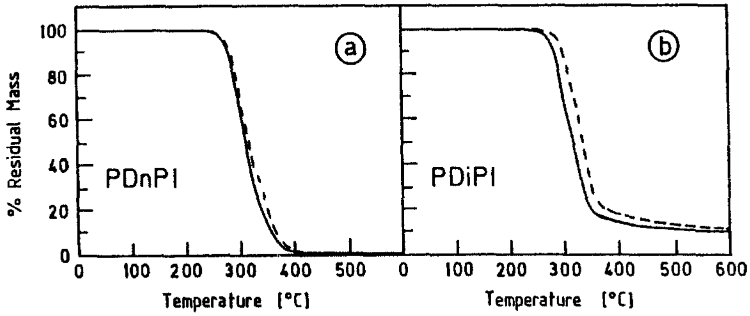

Fig. 2 TG curves for (a) PDnPI and (b) PDiPI. Volume DDM per 10 g monomer (—) 0 μL DDM, (— —) 100 μL DDM. Sample mass 2–3 mg. Heating rate 10°C min^{-1}. Nitrogen flow rate 20 cm^3 min^{-1}

Table 2 Characteristic mass loss temperatures, $T_{10\%}$, $T_{50\%}$ and $T_{90\%}$ and average apparent activation energies, E_a, for PDnPI and PDiPI in the mass loss range 5–60% and 5–75%, respectively

Polymer No.	Vol DDM/ μL	$T_{10\%}$	$T_{50\%}$	$T_{90\%}$	E_a/ kJ mol^{-1}
			°C		
N-1	0	279	309	355	101±3
N-2	5	279	308	356	104±4
N-3	10	282	311	361	115±5
N-4	25	280	310	359	113±3
N-5	50	284	316	361	107±5
N-6	100	284	318	364	101±3
I-1	0	281	316	–	141±4
I-2	5	280	315	–	116±4
I-3	10	281	318	–	119±4
I-4	25	282	320	–	118±3
I-5	50	283	320	–	120±2
I-6	100	297	335	–	115±3

PDnPI samples were approximately constant in the mass loss range 5–60%, after which they increased steadily. This trend has been found for other poly(di-*n*-alkyl itaconates) and explained by two initiation modes of depolymerisation, namely chain-end initiated and main-chain scission initiated depolymerisation [14]. In this work the studied polymers all had an even number of carbon atoms in the ester substituent, but it is hardly to be expected that an odd number of carbon atoms in the ester substituent would lead to a different degradation mechanism. On the other hand, the values of the E_a for PDiPI were constant from 5–75%, after which carbonisation occurred resulting in the 10% residue at 600°C. The average E_a values are given in Table 2 for all the polymer samples studied. The presence of DDM during the preparation of both the PDnPI and PDiPI samples had no effect on the E_a, at least within experimental error. The values of the E_a, averaged over all PDnPI and all PDiPI samples, were 107±6 kJ mol^{-1} and 118±2 kJ mol^{-1}, respectively.

The DTG curves, recorded at a heating rate of 10°C min^{-1}, for PDnPI and PDiPI prepared in the absence and presence of 100 μL DDM, respectively, are shown in Fig. 3a and b.

In the absence of DDM, the DTG curve of PDnPI agreed with those of other poly(di-*n*-alkyl itaconates) reported [14]. It has been shown that in the series poly(dimethyl-), poly(diethyl-), poly(di-*n*-butyl-), poly(di-*n*-hexyl-) and poly(di-*n*-octyl itaconate), the magnitude of the first peak decreases with increasing alkyl size and, simultaneously, the shoulder present in the lower members of the homologous series develops into a second peak. The first peak has been assigned to depolymerisation initiated by scission of the bond in the β-position to unsaturated chain ends. This peak is much larger than the peak of similar origin present in the DTG curves of poly(alkyl methacrylates) where chain-end unsaturation is introduced by polymerisation termination by disproportionation. The increased magnitude of the first peak in the poly(di-*n*-alkyl itaconates) has been explained by additional chain-end unsaturation being introduced into the polymer chains by chain transfer to monomer [14, 20]. It has been proposed that extensive chain transfer to monomer occurs during the polymerisation of itaconate monomers, due to the presence of the allylic group in their structure [3]. Also, the magnitude of the first DTG peak could be decreased by polymerising in the presence of DDM, the peak decreasing linearly in

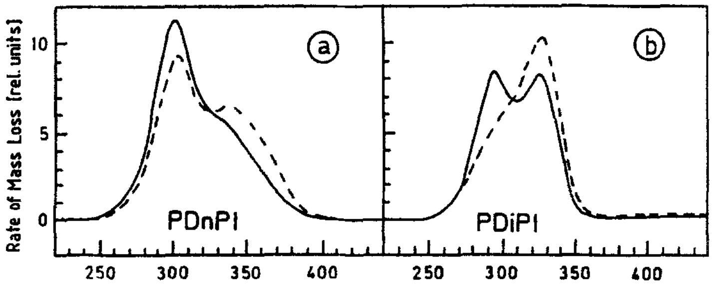

Fig. 3 DTG curves for (a) PDnPI and (b) PDiPI. Volume DDM per 10 g monomer (—) 0 μL DDM, (– –) 100 μL DDM. Sample mass 2–3 mg. Heating rate 10°C min^{-1}. Nitrogen flow rate 20 cm^3 min^{-1}

area with increasing DDM concentration. Chain termination by radical-radical annihilation and transfer to monomer are suppressed as chain transfer to DDM becomes the dominant chain termination process [21].

The degradation mechanism of PDiPI is more complex than that of PDnPI as, in addition to depolymerisation, ester decomposition occurs. This is evidenced by the presence of propene in the thermoanalysis volatiles, in addition to monomer, and carboxylic groups in the polymer residue. In the thermal degradation study of isomeric butyl esters of poly(methacrylic acid), Grassie showed that monomer is only released in the early stages of thermoanalysis of poly(*tert*-butyl methacrylate), after which ester decomposition occurs by a cyclic molecular mechanism whereby a hydrogen atom in the β-position to the carbonyl group is extracted [22, 23]. This, together with the similarity of the temperature of the first DTG maximum of poly(di-*n*-butyl-) (PDnBI) and poly(di-*sec*-butyl itaconate) (PDsBI) [18], would suggest that the first peak in the DTG curve of PDiPI results from chain-end initiated depolymerisation. The results of the effect of the presence of DDM during the polymerisation on the shape of the DTG curves confirms this conclusion because it is hardly possible for DDM to influence the structure of the ester group and subsequently the degradation mechanism. As with PDnPI, the presence of DDM must decrease the amount of end-chain unsaturation by competing with chain transfer to monomer.

The second peak in the DTG curve of PDiPI results from mass loss by reactions involving ester decomposition, whereas the second peak in the DTG curve of PDnPI is due to main-chain scission initiated depolymerisation. In this respect, the dialkyl esters of poly(itaconic acid) are qualitatively very similar to the alkyl esters of poly(methacylic acid) in their thermolysis behaviour, with the number of hydrogen atoms in the β-position to the carbonyl group determining the significance of the ester decomposition reaction. Thus, the thermal degradation of poly(methyl methacrylate), with no β-hydrogen atoms, yields monomer almost quantitatively [23], whereas only about 1% monomer is released during the thermal degradation of poly(*tert*-butyl methacrylate), which has nine β-hydrogen atoms [22]. Poly(*iso*-propyl methacrylate) (PiPMA), with six β-hydrogen atoms, represents an intermediate case in which both ester decomposition and depolymerisation are significant. Although no quantitative work has been performed to determine the amount of monomer released during the thermal degradation of PDiPI, it is to be expected that more monomer would be formed than during the thermal degradation of PiPMA, due to the extensive chain transfer to monomer expected during the polymerisation of DiPI. Chain transfer to monomer results in increased chain-end unsaturation and, hence, increased chain-end initiated depolymerisation.

In order to quantitatively determine the role of DDM during the polymerisation of DnPI and DiPI, the two peaks present in the DTG curves of both polymers were deconvoluted. The % error between the experimental DTG curve and the sum of the two deconvoluted peaks was no larger than 4%. As examples, the deconvoluted DTG curves of PDnPI prepared in the absence and presence of 100 μL DDM are shown in Fig. 4a and b, respectively, and the corresponding DTG curves for PDiPI are shown in Fig. 4c and d, respectively.

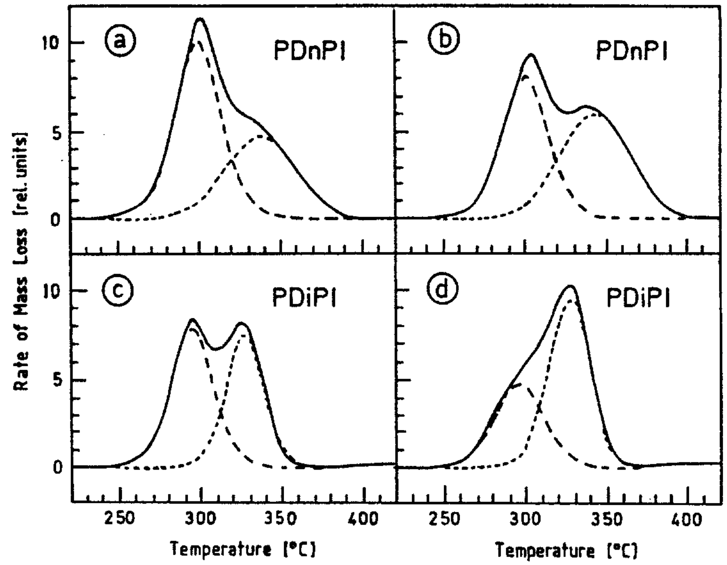

Fig. 4 DTG curves and deconvoluted DTG curves of (a) PDnPI prepared in the absence of DDM, (b) PDnPI prepared in the presence of 100 μL DDM/10 g monomer (c) PDiPI prepared in the absence of DDM, (d) PDiPI prepared in the presence of 100 μL DDM/10 g monomer. DTG curve (—), Peak 1 (– –) and Peak 1 (------). Heating rate 10°C min^{-1}, Sample mass 2–3 mg, Nitrogen flow rate 20 cm^3 min^{-1}

The areas of peaks 1 and 2 for each of the prepared polymers were calculated by integration and the relative area of the first peak calculated as the per cent of the total area. The influence of the amount of DDM present during the polymerisation of DnPI and DiPI is shown in Fig. 5, where the area of the first peak (as % of the total area) is plotted *vs.* the volume of DDM added per 10 g of monomer.

The slopes of the straight lines resulting in Fig. 5 give an estimate of the effectiveness of DDM, present during polymerisation, on the amount of monomer generated during the first stage of thermal degradation of the resulting polymers. Thus,

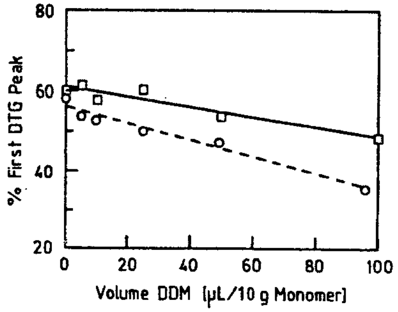

Fig. 5 Effect of the volume of DDM present during polymerisation on the % of peak 1 in the DTG curve of the resulting polymer. (—□—) PDnPI, (-o--o-) PDiPI

DDM is about 1.5 times more effective in decreasing the magnitude of the first DTG peak of PDiPI than the first DTG peak of PDnPI. There are three possible reasons for this. The first two reasons involve the absolute magnitudes of the chain-transfer-to-monomer constants and the chain-transfer-to-DDM constants. It is possible that the chain transfer to monomer is lower for DiPI than for DnPI due to the steric hindrance of access to the allylic hydrogen atoms. The third reason could be that a small amount of ester decomposition occurs simultaneously with the end-chain initiated depolymerisation process. It is known for the poly(alkyl methacrylates) that ester decomposition leads to the formation of, first, carboxylic acid groups and, then, anhydride groups and that depolymerisation cannot occur across the anhydride moieties [22]. This might also be the case with PDiPI, although the situation is slightly different because anhydride formation could occur on the same monomer unit and there is no logical reason why depolymerisation should not occur across such a structure.

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