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# The thermal degradation of poly(di-*n*-propyl itaconate) and poly(di-*iso*-propyl itaconate)

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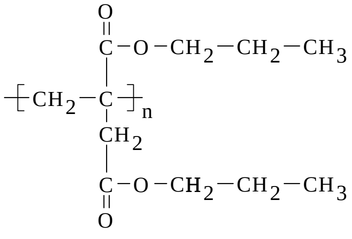
## Abstract

The non-oxidative thermal degradation mechanism of poly(di-*n*-propyl-) (PDnPI) and poly(di-*iso*-propyl itaconate) (PDiPI) were investigated and compared to the structurally similar polymethacrylates. Analogous to the corresponding polymethacrylates, PDnPI thermally decomposes predominantly by depolymerisation, whereas a considerable amount of side chain scission occurs during the thermal degradation of PDiPI. The thus formed carboxyl groups decarboxylate at elevated temperatures forming a carbonaceous residue. © 2000 Elsevier Science Ltd. All rights reserved.

*Keywords*: Thermal degradation; Poly(di-*n*-propyl itaconate); Poly(di-*iso*-propyl itaconate)

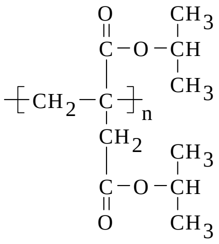
## 1. Introduction

The thermal degradation of alkyl esters of poly(methacrylic acid) has been extensively studied, especially by Grassie and coworkers [1,2]. However, after an initial paper [3] on the thermal degradation of polymers of di-*n*-alkyl esters of itaconic acid, only recently have details of the kinetics [4] and mechanisms [5,6] been published. All these studies were limited to *n*-alkyl esters. The kinetics of the thermal degradation of isomeric poly(dipropyl itaconate)s, poly(di-*n*-propyl-) (PDnPI) and poly(di-*iso*-propyl itaconate) (PDiPI) and of isomeric poly(dibutyl itaconate)s, poly(di-*n*-butyl-) (PDnBI), poly(di-*iso*-butyl-) (PDiBI) and poly(di-*sec*-butyl itaconate) have recently been reported [7]. The results obtained in this paper indicated that the mechanisms of thermal degradation of these polymers are different. In the present paper, details of the mechanism of the thermal degradation of PDnPI and PDiPI, the structures of which are given below, will be presented.



$-[CH_2-C(COO-CH_2-CH_2-CH_3)(CH_2-COO-CH_2-CH_2-CH_3)]_n-$

PDnPI



PDiPI

## 2. Experimental section

### 2.1. Chemicals

Di-*n*-propyl itaconate (DnPI) and di-*iso*-propyl itaconate (DiPI) were prepared by the standard acid-catalysed esterification of itaconic acid with 1-propanol and 2-propanol, respectively. The formed water was azeotropically removed from the system. Due to the high solubility of 2-propanol in water it was necessary to add excess alcohol in this case. After the normal work-up procedure, the monomers were vacuum distilled immediately prior to polymerisation. GC analysis indicated that the purity of the monomers was greater than 99%.

### 2.2. Method of polymerisation

Polymerisation was performed at 40°C in glass ampoules sealed under high vacuum using 0.5 mol% $\alpha,\alpha'$-isobisisobutyronitrile (AIBN) as initiator. The yields were kept to below 10% to ensure relatively narrow molar mass distributions. The polymers were isolated by precipitation with methanol containing about 5% water and made free of residual monomer by repeated precipitation from benzene

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solutions using methanol containing 5% water. The polymers were dried to constant mass at room temperature under vacuum.

### 2.3. Polymer characterisation

The molar masses of the undegraded polymers were measured by GPC using narrow molar mass PMMA samples as standards. The limiting viscosity numbers (LVN) of the samples were measured in toluene at 25°C using an Ubbelohde dilution viscometer.

### 2.4. Thermal degradation experiments

Thermal degradation experiments were performed using a small furnace, the temperature of which was controlled by a rheostat. The temperature of the furnace, measured by a Ni–NiCd thermocouple, was kept constant to ±1°C. Experiments were performed in the temperature range 220–280°C either under a nitrogen flow of 50 ml/min or under high vacuum. The sample masses ranged between 60 and 100 mg.

After determining the mass loss, the residues of the PDnPI degraded in a nitrogen flow were analysed by determining the LVN. The content of acid groups in the degraded polymer samples was measured by dissolving or swelling the residue in methanol, adding a known amount of methanolic 0.1 mol/l NaOH solution and back titrating the excess alkali with 0.1 mol/l HCl using phenolphthalein as indicator. IR spectra of the residues were recorded as films on NaCl plates using a Spekord 751R spectrometer.

The volatile products were measured on samples degraded under high vacuum. The total volume of gaseous products was measured using a Töppler pump and analysed by injecting the gas directly from the Töppler pump into a Varian 3400 gas chromatograph fitted with a thermal conductivity (TC) detector. A molecular sieve column, operating isothermally at 80°C, was used to qualitatively determine the amount of CO evolved, whereas a Porapak R column, operating isothermally at 30°C, was used to identify and qualitatively determine the amounts of $CO_2$, propene and propane present in the gaseous degradation products. Other instrument parameters were injection temperature 120°C, detector temperature 120°C, TC filament temperature 150°C. The carrier gas was argon or helium for the molecular sieve or Porapak R column, respectively.

Table 1
The LVN and molar mass of the polymers used in this study

| Polymer | LVN ($m^3$/kg) | Molar mass (g/mol) |
|---|---|---|
| PDnPI | 0.081 | $1.01 \times 10^{6}$[a] |
| PDiPI | 0.051 | – |

[a] $K$ and $a$ values from Ref. [12].

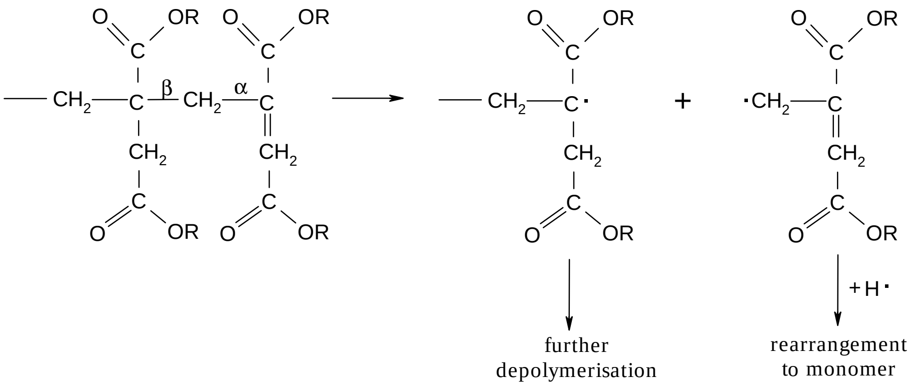
## 3. Results and discussion

The initial molar masses, as determined by GPC, and the LVNs of the polymers used in this study are given in Table 1.

### 3.1. Thermal degradation of PDnPI

The isothermal mass loss as a function of degradation time at various degradation temperatures is shown in Fig. 1.

It has been established previously that the main degradation mechanism of poly(di-*n*-alkyl itaconates) with ester substituents having an even number of carbon atoms is depolymerisation [5]. It is hardly to be expected that ester substituents with an odd number of carbon atoms would lead to a fundamentally different degradation route. Monomer was indeed identified as a thermal degradation product of PDnPI, but the amount was not quantitatively determined. Thermogravimetry has shown that monomer evolution occurs in two stages, indicating the two major modes of depolymerisation by end chain scission and random main chain scission. The end chain scission occurring at the β-bond to a terminal double bond is the lower temperature process. The terminal double bonds originate not only from termination by disproportionation but also, from chain transfer to monomer during radical polymerisation.



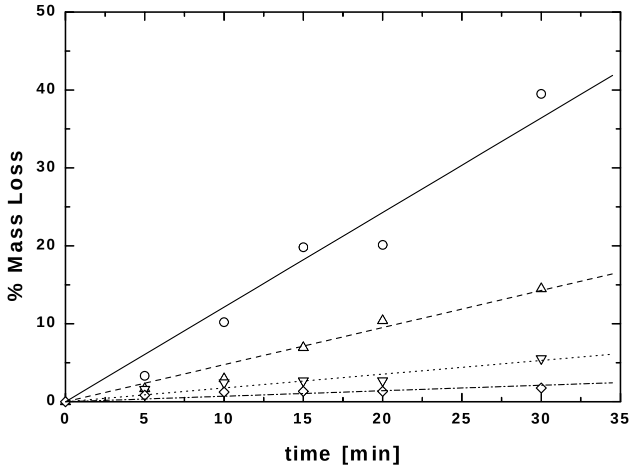


Fig. 1. Mass loss as a function of time for PDnPI thermally heated at various temperatures, (–○–) 280°C, (--△--) 260°C, (··▽···) 240°C and (-··◇-··-) 220°C.

The molar masses of the degradation residues as a function of time at different temperatures are shown in Fig. 2a and the relative change in molar mass as a function of mass loss in Fig. 2b. Both sets of diagrams show that the molar masses decrease considerably during degradation. The shapes of the $\bar{M}_W/\bar{M}_{W,O}$ vs. conversion curves indicate the occurrence of random main chain scission and/or that the zip length ($Z$) is smaller than the degree of polymerisation of the polymer.

An attempt was made to calculate the zip length of depropagation by the equation proposed by Kashiwagi et al. [8]:

$$\frac{W}{W_0} = \frac{\bar{P}_n^2}{\bar{P}_0^2}\left(\frac{Z+\bar{P}_0}{Z+\bar{P}_n}\right)$$

where $W/W_0$ is the ratio of the mass of the residue and the mass of the initial polymer and $\bar{P}_0$ and $\bar{P}_n$ are the degrees of polymerisation of the initial and degraded polymer, respectively. This calculation takes into consideration only the chain reaction of depropagation with the exclusion of chain transfer reactions. The results of the calculations are presented in Fig. 3. which shows the temperature and time dependence of $Z$. Compared to the results of similar calculations for PMMA degraded in the temperature range 260–300°C, which gave $Z$ values between 1000 and 2000 [9], the values of $Z$ calculated for PDnPI are very low. Very low values of $Z$ for other poly(di-*n*-alkyl itaconates) have also been determined [6]. The hydrogen atoms of the side chain $CH_2$ groups can be considered as labile due to the C=O group in the β-position. Chain transfer to these hydrogen atoms can occur thus terminating the depropagation of a particular polymer chain. Thus, the values of $Z$ can only be considered as apparent as they can in no way represent the kinetic zip length as depropagation continues after transfer to polymer.

It is possible to determine the number of main chain scissions per monomer unit on the basis of changes in the mass and molar mass of the degraded sample [10]. The number of bond scissions per monomer unit, $s/P_0$, can be calculated from the equation [10]:

$$\frac{s}{P_0} = \frac{1-x}{P_t} - \frac{1}{P_0}$$

where $s$ is the number of scissions and $x$ is the fraction of evaporated thermolysis volatiles. The results of this calculation are shown in Fig. 4 where $s/P_0$ is plotted against time at various temperatures.

As can be seen the number of bonds broken per monomer unit increases linearly with degradation time as is to be expected and is higher the higher the degradation temperature.

The value of $s/P_0$ determined in this paper for PDnPI after a degradation time of 30 min at 260°C compares very well

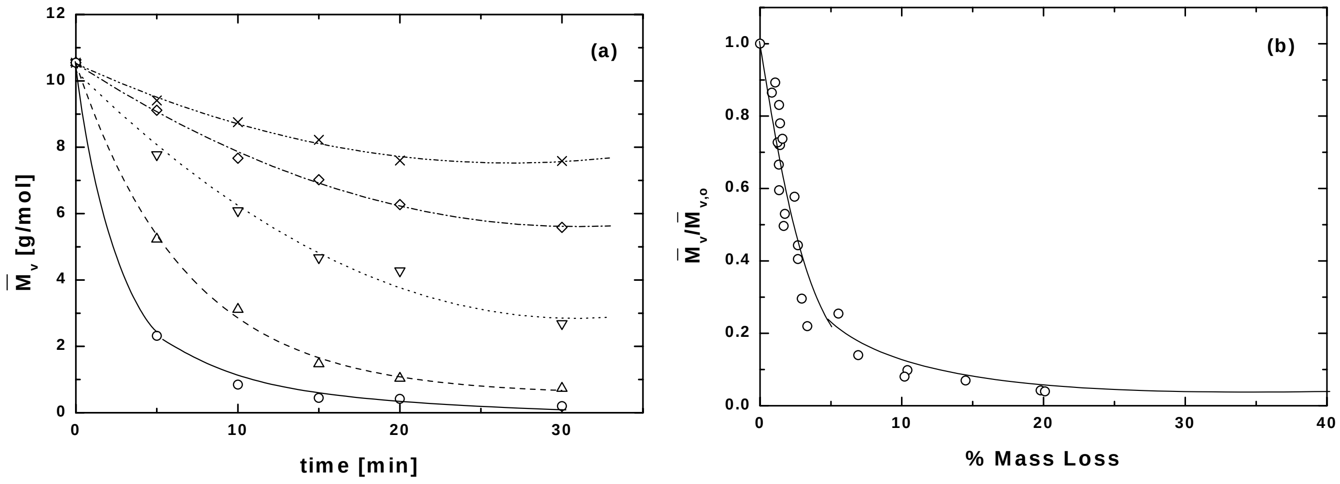


Fig. 2. (a) Viscosity average molar mass ($M_v$) of PDnPI as a function of time, (–○–) 280°C, (--△--) 260°C, (··▽···) 240°C, (-··◇-··-) 220°C and (-··×-··-) and (b) relative change in the viscosity average molar mass ($M_v/M_{v,o}$) as a function of mass loss after thermal treatment.

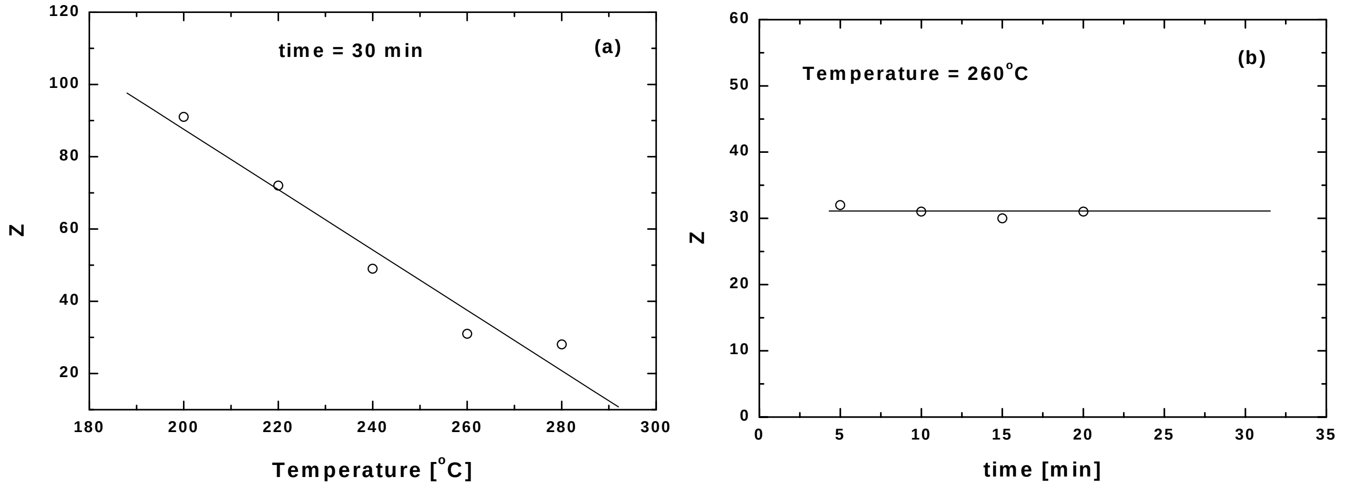


Fig. 3. Dependence of the apparent depolymerisation zip length ($Z$) on (a) temperature after a thermolysis time of 30 min and (b) time at a thermolysis temperature of 260°C.

with values obtained for other poly(di-*n*-alkyl itaconates) after degradation under the same conditions (see Fig. 5) [6]. Thus, the results obtained in this work confirm that, in the series of poly(di-*n*-alkyl itaconates), the value of $s/P_0$ increases linearly with the number of C atoms in the ester substituent.

### 3.2. Thermal degradation of PDiPI

The dependance of the mass loss for PDiPI on degradation temperature and time are shown in Fig. 6a and b, respectively. As can be seen from Fig. 6, the mass loss increases rapidly above 240°C and increases linearly with time. Attempts to determine the LVN of the degraded polymers were not successful as $\eta_{sp}/c$ increased with decreasing polymer concentration. This behaviour indicates that the structure of the polymer residue changes during thermal degradation implying that depropagation is not the only degradation mechanism occurring and that the polymer residue has ionomeric properties in dilute solution.

The IR spectrum of the residue of a sample degraded at 280°C for 30 min as well as that of the undegraded polymer are shown in Fig. 7a and b, respectively. The spectrum of the degraded polymer shows two new carbonyl bands at 1767 and 1826 $\text{cm}^{-1}$ not present in the spectrum of the undegraded sample. These bands are characteristic of the carbonyl groups of an anhydride structure.

The anhydride structures were determined quantitatively by acid–base titrations of the residues. The determined amounts of anhydride groups, expressed as mol COOH per base mol are shown as a function of degradation time and temperature in Fig. 8a and b, respectively.

Grassie has shown that, in the case of polymethacrylates, ester decomposition leading to the formation of acid groups in the polymer chain occurs by a cyclic mechanism which also results in the simultaneous formation of the corresponding

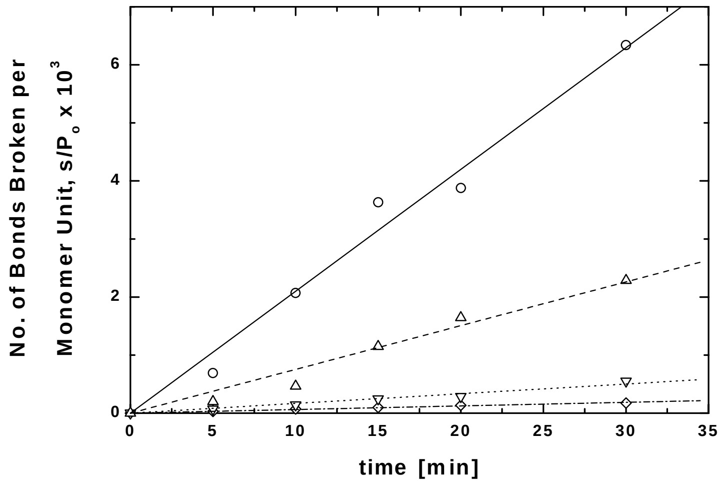
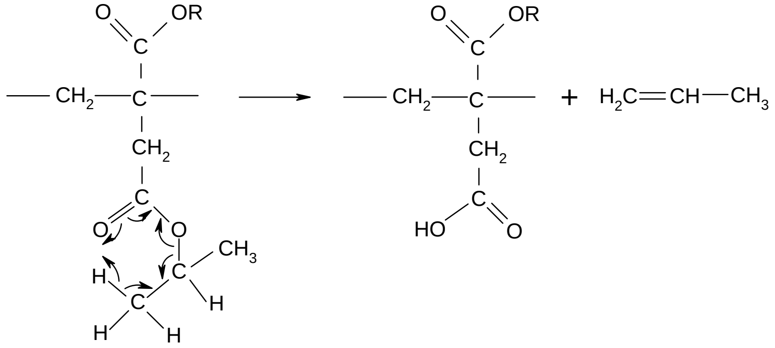


Fig. 4. Dependence of the number of bonds broken ($s/P_0$) on time at various thermolysis temperatures, (–○–) 280°C, (--△--) 260°C, (··▽···) 240°C and (-·-◇-·-) 220°C.

alkene [2]. He also demonstrated that the significance of this ester decomposition reaction depends on the number of H-atoms in the β-position to the carbonyl group [11]. If this reaction, shown below, occurs in the itaconate class of polymers, then ester decomposition during the thermal degradation of PDiPI should lead to the formation of propene.

The determined amounts of propene evolved as a function of degradation time and temperature are shown in Fig. 9a and b, respectively.



Also shown in Fig. 9 are the amounts of $CO_2$ evolved during thermal degradation. The amounts of both gases evolved were always very similar, although there was always more $CO_2$ than propene. The amounts of both gases increase linearly with time but exponentially with temperature. Propane was also identified in the degradation products, although the amounts were much smaller than the amounts of propene. The formation of propane would also lead to the simultaneous formation of $CO_2$, hence the slightly larger amounts of $CO_2$ than propene. At 280°C the amount of propene evolved is about 300 times the amount of COOH groups found in the polymer residue. Obviously secondary reactions occur during thermal degradation as evidenced by the amount of $CO_2$ found in the degradation products. The $CO_2$ probably arises from decarboxylation of the carboxylic acid groups formed. As only anhydride groups were evidenced in the IR spectra of the degradation residues, dehydration probably competes with decarboxylation of the carboxylic acid groups formed during propene elimination and only the anhydride groups remain in the polymer residue. The anhydride groups are the precursors to the carbonaceous residue formed remaining after heating the polymer to 600°C during thermogravimetric analysis [12].

The amount of CO formed was more than two orders of magnitude smaller than the amount of $CO_2$ generated. During the degradation of poly(di-*n*-alkyl itaconate)s it has been shown that more $CO_2$ is generated than CO and that the ratio is about 10:1 [5].

At all degradation temperatures monomer is one of the main degradation products, indicating that depolymerisation is a major degradation route. Thermogravimetric analysis of PDiPI has shown that this polymer degrades in two stages. The first mass loss step was ascribed to chain end initiated depolymerisation and the second to ester decomposition. The amount of monomer generated in the second mass loss stage is unknown but, based on the amount of propene and $CO_2$ generated, combined with the amount of carbonaceous

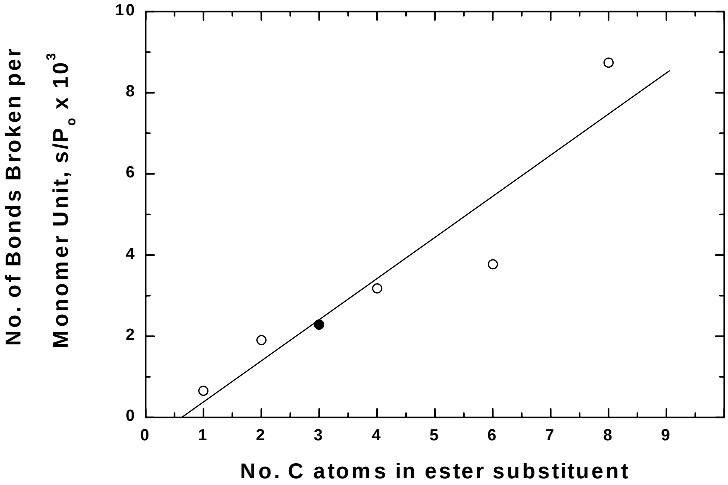


Fig. 5. Dependence of the number of bonds broken ($s/P_0$) on the number of carbon atoms in the ester substituent, (●) this work and (○) from Ref. [6]. Degradation temperature 260°C, degradation time 30 min.

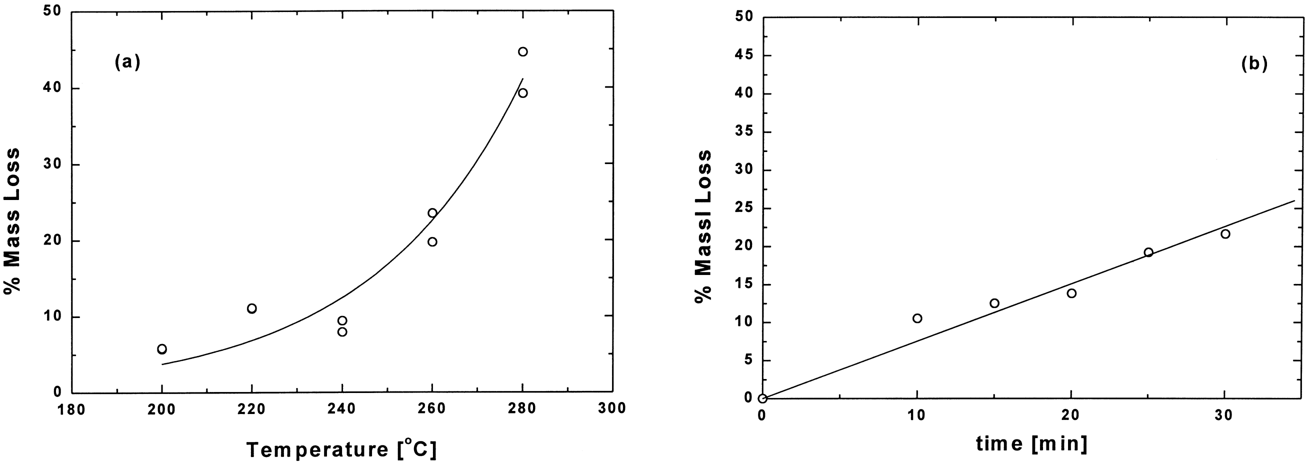


Fig. 6. Mass loss as a function of: (a) temperature for PDiPI thermally heated for 30 min; and (b) time at a thermolysis temperature of 260°C.

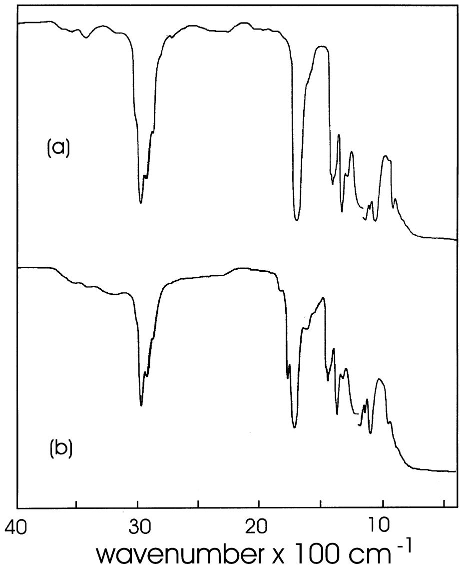


Fig. 7. IR spectrum of a PDiPI (a) before and (b) after heating at 280°C for 30 min.

residue, the second mass loss stage must be almost completely due to the generation of gaseous products with very little side or main chain scission initiated depolymerisation occurring. Work is at present in progress to clarify this point.

## 4. Conclusions

Poly(di-*n*-propyl itaconate) thermally degrades predominately by depolymerisation, monomer being the main degradation product. The monomer is generated in two stages, by chain end initiated and main chain scission initiated depropagation. As with other poly(di-*n*-alkyl itaconate)s, the values of the zip length of depropagation are much shorter than values determined for poly(methyl methacrylate), less than 100 as compared to between 1000 and 2000 for PMMA. The zip length decreases slightly with increasing temperature.

Poly(di-*iso*-propyl itaconate) thermally degrades by depolymerisation and ester decomposition. At temperatures below about 250°C the main process is depolymerisation

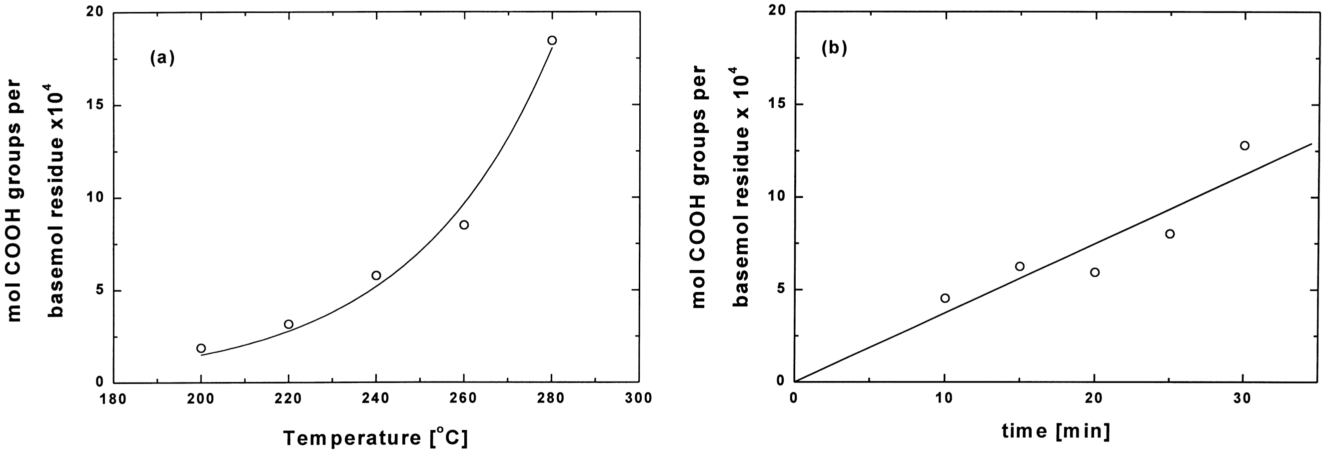


Fig. 8. Moles COOH groups per basemol PDiPI residue as a function of (a) thermolysis temperature, exposure time 30 min and (b) exposure time at 260°C.

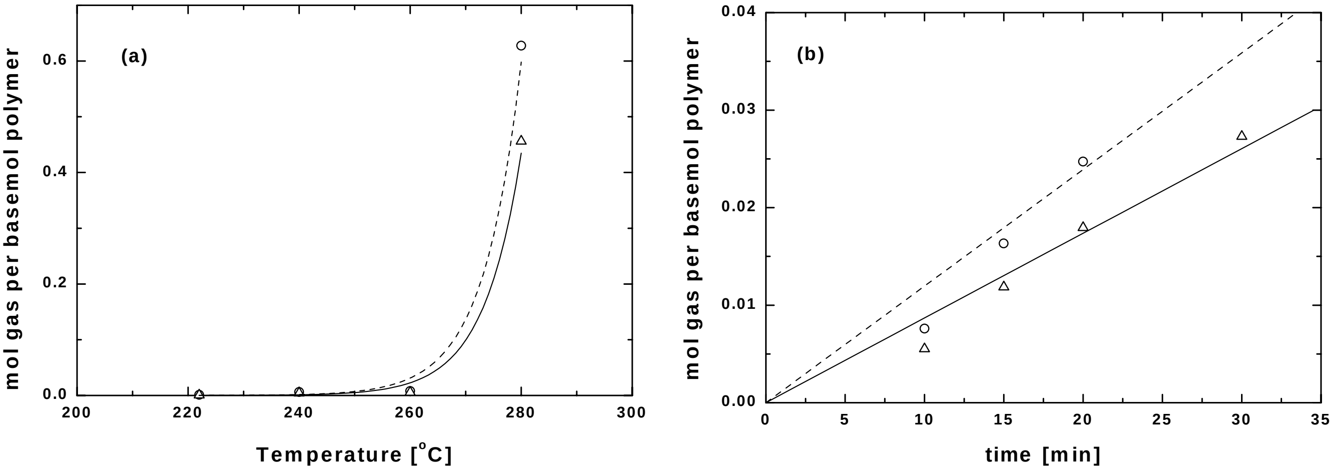


Fig. 9. Moles evolved $CO_2$ (○) and propene (Δ) per base mol PDiPI as a function of: (a) thermolysis temperature, exposure time 30 min and (b) exposure time at 260°C.

with ester decomposition being the dominant process at higher temperatures. The amount of depolymerisation is thought to be higher than during the thermal degradation of poly(*iso*-propyl methacrylate) due the presence of a larger number of chains having unsaturated chain ends in the polymer, the main source of chain end unsaturation being chain transfer to monomer during polymerisation.

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