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THE NON-OXIDATIVE THERMAL DEGRADATION OF POLY(DI-2-CHLOROETHYL ITACONATE)

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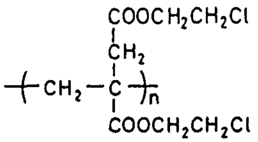
The non-oxidative thermal degradation of poly(di-2-chloroethyl itaconate) (PD2CEI) was studied by TG and by analysing the thermal products. The major processes occurring during thermal analysis are crosslinking, depolymerisation and carbonisation. The thermal degradation activation energy increased with increasing sample mass loss. The thermal degradation of PD2CEI was compared to that of the structurally similar poly(2-chloroethyl methacrylate) (P2CMA).

Keywords: kinetics, non-oxidative thermal degradation, poly(di-2-chloroethyl itaconate)

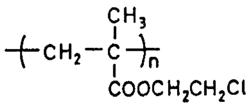
Introduction

Poly(di-*n*-alkyl itaconates) predominantly degrade thermally by depolymerisation [1–3]. The introduction of a chlorine atom into the ester substituent affects the thermolysis mechanism as already established in the case of poly(2-chloroethyl methacrylate) (P2CMA) [4]. The purpose of this study was to investigate the non-oxidative thermal degradation kinetics and mechanism of poly(di-2-chloroethyl itaconate) (PD2CEI) (I) and to compare them to the structurally similar P2CMA (II).



$$\left[CH_2-\underset{\underset{COOCH_2CH_2Cl}{|}}{\overset{\overset{\overset{COOCH_2CH_2Cl}{|}}{CH_2}}{\overset{|}{C}}} \right]_n$$

(I)



$$\left[CH_2-\underset{\underset{COOCH_2CH_2Cl}{|}}{\overset{\overset{CH_3}{|}}{C}} \right]_n$$

(II)

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Experimental

PD2CEI was obtained by bulk polymerisation at 35°C with 0.9 mol% α,α'-azobisisobutyronitrile (AIBN) as initiator. The weight average molar mass of the initial polymer was determined by light scattering measurements (Brice Phoenix instrument) and found to be 1.33×10^6 g·mol^{-1}.

Thermogravimetric measurements were performed using a Perkin Elmer TGS-2 instrument in the temperature range 30° to 500°C at heating rates of 0.625, 2.5, 10, 20 and 40 deg·min^{-1}. The average sample mass was 5 mg and the nitrogen flow rate 25 cm^3·min^{-1}. The overall thermal degradation activation energies, E_a, were determined by the Flynn-Wall method [5].

The thermal degradation set-up and characterisation of thermolysis products were the same as in earlier studies [4, 6].

Results and discussion

Characteristic non-oxidative TG curves are shown in Fig. 1. The slopes of the TG curves are heating rate dependent, as is the amount of carbonaceous residue. At higher heating rates, the TG curves are steeper and there is less residue.

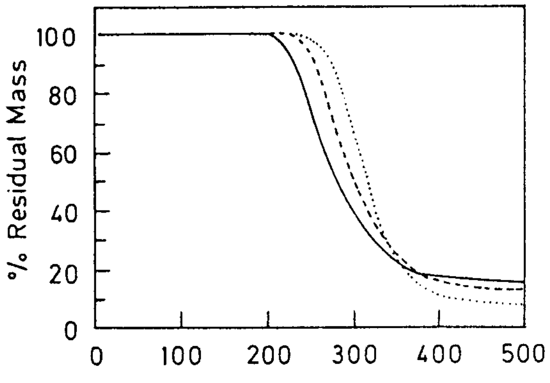

Fig. 1 Characteristic TG curves of PD2CEI, heating rates 0.625 (——), 10 (– – –) and 40 deg·min^{-1} (······), N_2 flow rate 25 cm^3/min

PD2CEI readily crosslinks at low temperatures. Initial crosslinking tendencies were registered at 100°C by an increase in the limiting viscosity number (LVN) and the first signs of gel were detected at 150°C (Fig. 2). It may be assumed that crosslinking is initiated by reactions in the side chains as manifested by a decrease in the carbonyl content of the degraded polymer. This loss of carbonyl groups was followed by means of the change in the ratio of the intensity of characteristic IR absorption bands of the carbonyl stretching frequency at 1729 cm^{-1} and the aliphatic C–H stretching band at 2932 cm^{-1}, E_{1729}/E_{2932} (Fig. 3). In the case of P2CMA the evolution of HCl [7] as well as other minor volatile degradation products, led to the conclusion that dehydrochlorination was the first step in a series of reactions leading to crosslinking and further degradation. Due to the same ester substituents in the side chains, it is assumed that the thermal degradation of PD2CEI is initiated in a similar manner.

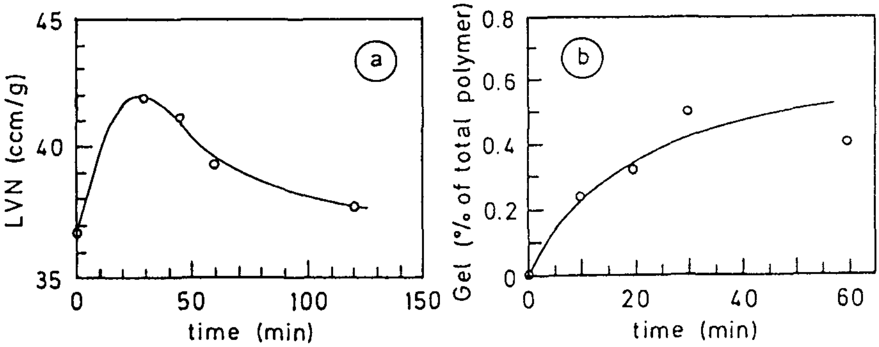

Fig. 2 Changes in the residue: a) LVN at 100°C and b) amount of gel (% of initial polymer) at 150°C with degradation time

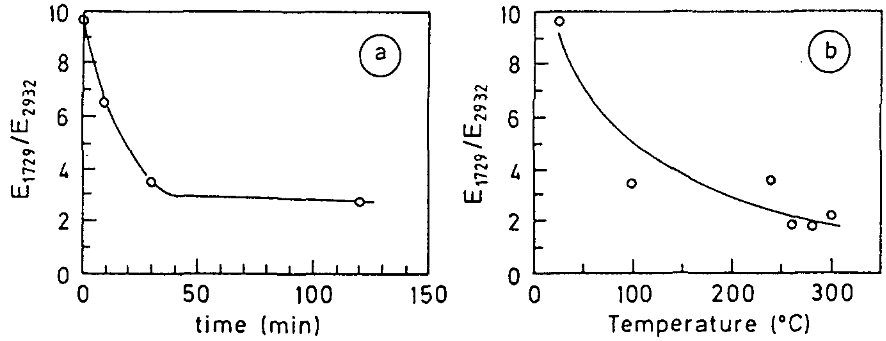

Fig. 3 Changes in the residue: E_{1729}/E_{2932} as a function of a) degradation time at 100°C and b) temperature, degradation time 30 minutes

As the temperature increases, crosslinking continues to be the favoured reaction up to about 240°C, when relevant polymer mass loss is registered, and depolymerisation becomes the major degradation reaction. The strong affinity toward crosslinking can be related to the existence of two substituents in the monomer unit capable of initiating crosslinking, as opposed to only one in the case of P2CMA (Fig. 4a).

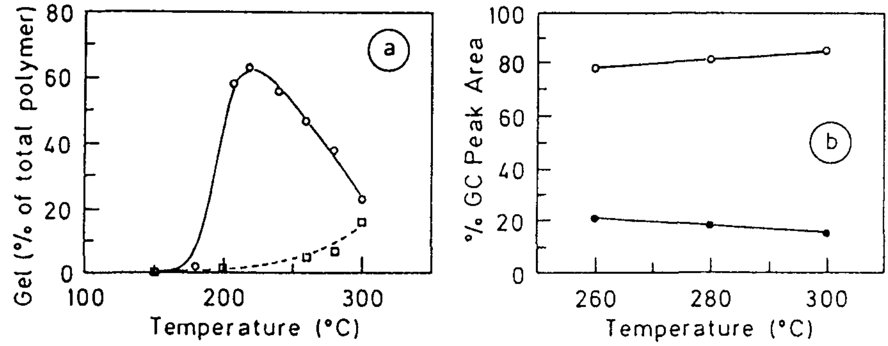

Fig. 4 a) Dependence of the amount of gel (% of initial polymer) on temperature, degradation time 30 minutes, PD2CEI (o), P2CMA (□), b) Dependence of the amount of evolved volatiles on temperature, degradation time 30 minutes, monomer (o), other volatiles (•)

Depolymerisation competes with crosslinking in the temperature interwal 240° to 280°C. As the temperature increases, the amount of volatile products resulting from side chain scission is decreased, implying the dominance of the initiation of depolymerisation by main chain scission (Fig. 4b). At temperatures greater than 280°C the residual crosslinked structures start to carbonise.

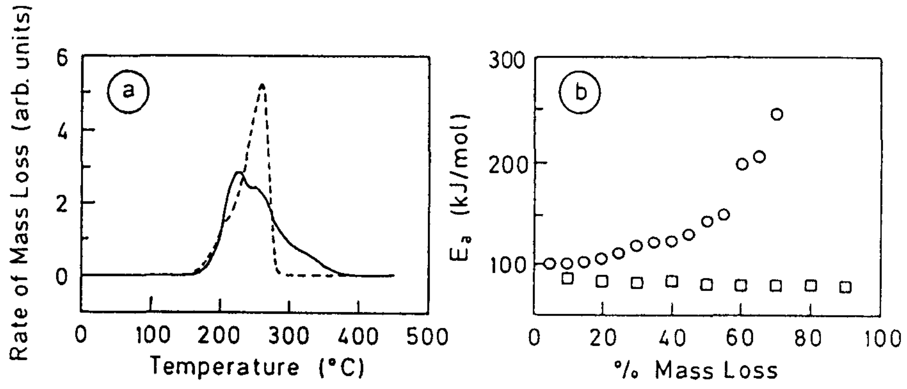

Fig. 5 a) DTG curves of PD2CEI (—) and P2CMA (---), heating rate 0.625 deg·min^{-1}, b) dependence of the E_a's on polymer mass loss, PD2CEI (o), P2CMA (□)

The complexity of the differential TG curve of PD2CEI, as compared to that of P2CMA [4] (Fig. 5a), is probably a consequence of the increased tendency of PD2CEI to crosslink and the competition of the three consecutive, partly overlapping processes: crosslinking, depolymerisation and carbonisation.

The overall thermal degradation activation energies also indicate the changing mechanism as the values of E_a increase considerably with polymer mass loss (Fig. 5b). In the case of P2CMA, where crosslinking is not a major thermolysis reaction and there is no carbonisation, the E_a's are independent of mass loss and can be related predominantly to depolymerisation.

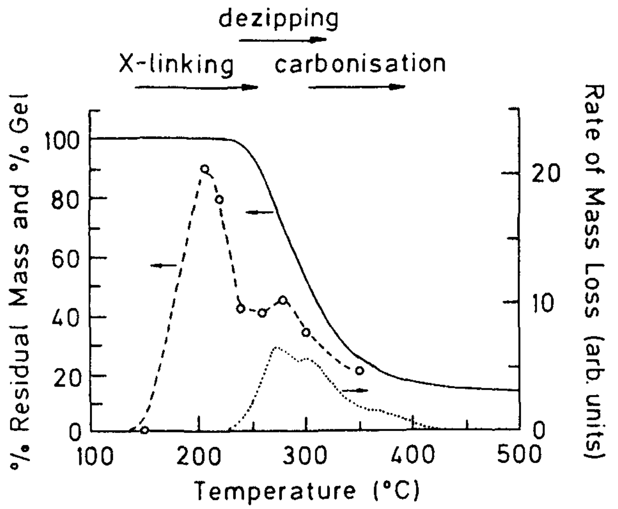

Fig. 6 Overall non-oxidative thermal degradation scheme of PD2CEI, TG (—) and DTG (---) curves, heating rate 0.625 deg·min^{-1}, amount of gel formed (% of initial polymer) (--o--), degradation time 45 minutes

A combined presentation of the processes occurring during the thermal degradation of PD2CEI is shown in Fig. 6. The start of significant mass loss on the TG curve coincides with a decrease in the amount of gel formed. The first DTG peak coincides with the saddle in the gel content curve indicating extensive depolymerisation. The second DTG peak or plateau corresponds to the second, smaller maximum of formed insoluble product which can be correlated to simultaneous depolymerisation and initial carbonisation. At higher temperatures the dominant thermolysis process is carbonisation.

Conclusions

Although the volatile thermal products of poly(di-2-chloroethyl itaconate) are analogous to those of poly(2-chloroethyl methacrylate), because of the occurrence of extensive crosslinking due to the itaconate derivative being a diester, the thermal degradation is much more complex. The complexity manifests itself primarily in the shape of the DTG curve which can be explained in terms of three significant, partly overlapping, processes: crosslinking, depolymerisation and carbonisation.

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Zusammenfassung —Mittels TG und der Analyse der thermischen Produkte wurde der nichtoxidative Abbau von Poly(di-2-chlorethyl-itakonat) (PD2CEI) untersucht. Die bei der Thermoanalyse ablaufenden Hauptprozesse sind Vernetzung, Depolymerisation und Karbonisierung. Die Aktivierungsenergie des thermischen Abbaues steigt mit zunehmenden Massenverlust der Probe. Der thermische Abbau von PD2CEI wurde mit dem des strukturähnlichen Poly(2-chlorethyl-methacrylat) (P2CMA) verglichen.