

POLY(DIALKOXYETHYL ITACONATES)

II. The thermal degradation of some poly(dialkoxyethyl itaconates)

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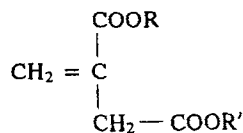
Abstract

The oxidative and non-oxidative degradation of poly(di-methoxy-), poly(di-ethoxy-), poly(di-*iso*-propoxy-) and poly(di-*n*-butoxyethyl itaconate) were investigated by thermogravimetry. Characteristic degradation temperatures and apparent activation energies of degradation were determined for the non-oxidative degradation of all the investigated polymers. It was not possible to determine these characteristics in the presence of oxygen as the degradation was accompanied by a secondary exothermic reaction. Based on examination of the monomers, it is supposed that the exothermic reaction is a repolymerisation of the monomers released during the earlier stages of polymer degradation.

Keywords: poly(dialkoxyethyl itaconates), thermal degradation, thermogravimetry

Introduction

Itaconic acid, i.e. methylene succinic acid, is an interesting starting compound for the synthesis of a wide variety of polymeric materials. Thus, it is possible to synthesize both di- and monoesters, as well as mixed di-esters of the following general formula



where *R* and *R'* can be a hydrogen atom or an alkyl, alicyclic or aromatic group. Due to the variety of ester substituents, polymers based on itaconic acid can be tailor-made by changing the ester substituents.

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The synthesis [1–3], solid state [4] and solution properties [5–7], as well as the thermal stability [8–13] of the di-*n*-alkyl esters of itaconic acid have been well studied. Papers concerning the synthesis and characterisation of di-etheric esters of poly(itaconic acid) have been published [14–16]. These polymers have methyl terminated poly(ethylene oxide) side chains of varying lengths. The homologous series with alkoxyethyl ester groups, which also have etheric ester groups, has, however, received little attention. Some work [17] has been performed on the poly(mono-alkoxyethyl itaconates), where only one of the carboxylic groups is esterified, but to the best of our knowledge only the dimethoxyethyl ester, being the first member of both the di(polyethylene oxide) and the di-alkoxyethyl homologous series, has been reported in the literature [16, 18]. This work is a continuation of our work on the poly(di-alkoxyethyl itaconate) homologous series and the first dealing with the thermal properties of this family of polymers.

Experimental

The polymers, poly(di-methoxy-) (PDMOEI), poly(di-ethoxy-) (PDEOEI), poly(di-isopropoxy-) (PDPOEI) and poly(di-*n*-butoxyethyl itaconate) (PDBOEI) were prepared by the AIBN initiated bulk polymerisation of the corresponding monomer. Details of the polymerisation conditions are given in Table 1.

The molar masses of the polymers were measured by light scattering in ethyl methyl ketone at 25°C using a Brice Phoenix OM-2000 Light Scattering Pho-

Table 1 Polymerisation conditions, molar mass and LVN of the used polymers

| Polymer | AIBN/ mol% | T_{pol} / °C | Time/ h | Yield/ % | LVN/ ($m^3 kg^{-1}$) $\times 10^2$ | \bar{M}_w / ($g mol^{-1}$) $\times 10^{-5}$ |
|-----------|---------------|-------------------|------------|-------------|---|--|
| PDMOEI-40 | 0.5 | 40 | 17 | 18.4 | 4.00 | 9.62 |
| PDMOEI-50 | 0.5 | 50 | 6.5 | 17.2 | 2.85 | 5.67 |
| PDMOEI-60 | 0.5 | 60 | 4 | 20.8 | 1.73 | 5.02 |
| PDEOEI-40 | 0.5 | 40 | 17 | 19.2 | 4.12 | 9.71 |
| PDEOEI-50 | 0.5 | 50 | 6.5 | 19.8 | 2.71 | 6.25 |
| PDEOEI-60 | 0.5 | 60 | 4 | 17.2 | 2.19 | 2.96 |
| PDPOEI-40 | 0.5 | 40 | 24 | 22.0 | 4.89 | 10.80 |
| PDPOEI-50 | 0.5 | 50 | 3 | 5.44 | 4.27 | 8.97 |
| PDPOEI-60 | 0.5 | 60 | 2.25 | 3.21 | 2.86 | 7.46 |
| PDBOEI-40 | 0.5 | 40 | 18.5 | 20.1 | 4.63 | 7.81 |
| PDBOEI-50 | 0.5 | 50 | 4.5 | 9.0 | 3.25 | 4.94 |
| PDBOEI-60 | 0.5 | 60 | 3.5 | 15.1 | 2.27 | 3.46 |

tometer operating with 436 nm light. The limiting viscosity numbers (LVN) were measured in toluene at 25°C using an Ubbelohde dilution viscosimeter.

Non-isothermal thermogravimetry was performed in a nitrogen flow (22 cm³ min⁻¹) using a Perkin Elmer TGS-2 instrument equipped with a FDS for the simultaneous measurement of the differential TG curves. The non-oxidative degradation experiments were performed at heating rates of 2.5, 10, 20 and 40°C min⁻¹. The average sample mass was 5 mg. The oxidative runs were performed using an air flow rate of 15 cm³ min⁻¹ and a heating rate of 10°C min⁻¹. In these cases the sample masses were also about 5 mg except where stated otherwise.

Differential scanning calorimetry (DSC) was performed in open aluminium pans under an air flow of 25 cm³ min⁻¹ at a heating rate of 10°C min⁻¹ with a Perkin Elmer DSC-2 instrument. The average sample mass was 20 mg.

Results and discussion

The molar masses and LVN of the prepared polymers are given in Table 1.

Typical non-oxidative thermogravimetric (TG) curves for the four polymers, prepared at 40°C are shown in Figs 1a-d. For all polymers, within experimental error, the shapes of the curves were independent of the molar mass of the polymer in the range studied.

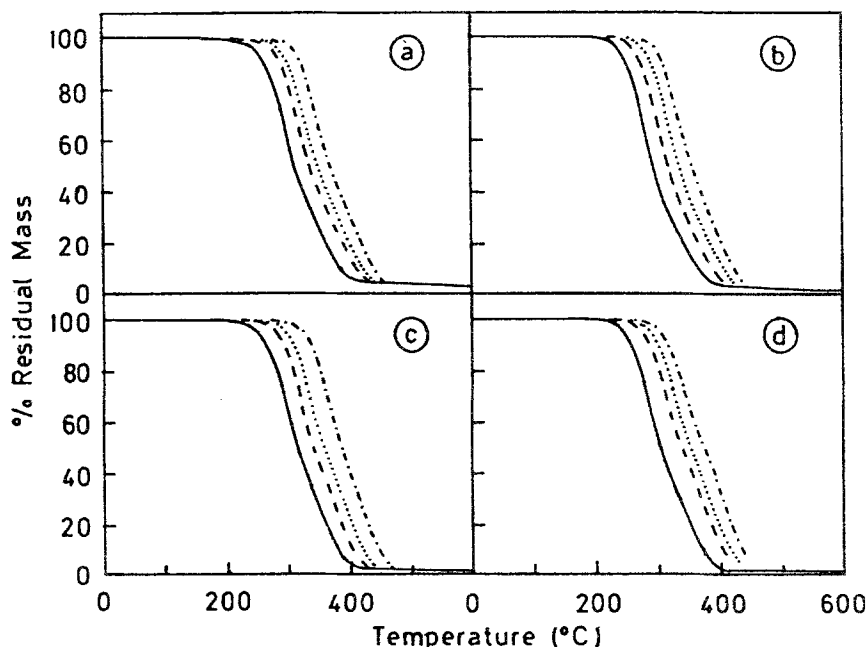


Fig. 1 Non-oxidative TG curves of poly(dialkoxyethyl itaconates), a) PDMOEI, b) PDEOEI, c) PDPOEI and d) PDBOEI, heating rate 2.5 (—), 10 (---), 20 (....), 40°C min⁻¹ (- · - · -), nitrogen flow rate 22 cm³ min⁻¹

Table 2 Characteristic temperatures of the non-oxidative TG curves of poly(dialkoxyethyl itaconates), heating rate $2.5^{\circ}\text{C min}^{-1}$, nitrogen flow rate $22\text{ cm}^3\text{ min}^{-1}$

| Polymer | $T_{10\%}/^{\circ}\text{C}$ | $T_{50\%}/^{\circ}\text{C}$ | $T_{90\%}/^{\circ}\text{C}$ | Residue _{600°C} /% |
|-----------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|
| PDMOEI-40 | 253.3 | 299.0 | 371.3 | 3.0 |
| PDMOEI-50 | 251.8 | 298.0 | 370.0 | 2.0 |
| PDMOEI-60 | 258.8 | 308.0 | 381.8 | 3.2 |
| PDEOEI-40 | 250.5 | 292.0 | 365.0 | 1.5 |
| PDEOEI-50 | 249.0 | 293.3 | 368.5 | 1.5 |
| PDEOEI-60 | 252.0 | 303.0 | 375.8 | 2.5 |
| PDPOEI-40 | 252.5 | 303.0 | 366.5 | 0.7 |
| PDPOEI-50 | 254.5 | 300.0 | 370.0 | 2.0 |
| PDPOEI-60 | 257.5 | 303.0 | 372.5 | 1.2 |
| PDBOEI-40 | 256.3 | 302.5 | 371.0 | 0.5 |
| PDBOEI-50 | 259.2 | 310.6 | 375.1 | 1.2 |
| PDBOEI-60 | 258.0 | 305.0 | 377.5 | 1.5 |
| PDBI* | 248.3 | 277.3 | 321.0 | 2.0 |
| PDHI* | 241.8 | 285.3 | 334.8 | 2.0 |

*Ref. [11]

Characteristic non-oxidative thermal degradation temperatures, expressed as the temperatures of 10, 50 and 90% mass loss, $T_{10\%}$, $T_{50\%}$ and $T_{90\%}$, respectively, as well as the percent residue at 600°C are given in Table 2. For comparison, corresponding literature [11] values for poly(di-*n*-butyl-) (PDBI) and poly(di-*n*-hexyl itaconate) (PDHI) are included in the table.

The apparent activation energies of mass loss, E_a , for all the studied polymers were calculated at 10% mass loss intervals from the sets of TG curves recorded at 2.5 , 10 , 20 and $40^{\circ}\text{C min}^{-1}$ using the Flynn-Wall method [19]. The obtained values are presented in Table 3 from which it can be seen that, within experimental error, the E_a s are independent of molar mass of the polymers and, furthermore, independent of the ester substituent. In all cases a first stage up to about 60% mass loss with an E_a of about 94 kJ mol^{-1} was found, followed by a second stage from 60–90% with an E_a of about 120 kJ mol^{-1} . In the case of poly(methyl methacrylate), PMMA, prepared by radical polymerization, the E_a is dependent on the molar mass of the polymer increasing with molar mass [20]. This dependence has been explained by weak links and chain end unsaturation, introduced during biradical polymerisation termination by disproportionation, the scission of which initiates depolymerisation. Hence, the lower the molar mass the greater the concentration of weak structures in the polymer. In

Table 3 Apparent activation energy, E_a , and average E_a , \bar{E}_a , of the non-oxidative thermal degradation of the studied poly(dialkoxyethyl itaconates) as determined at 10% mass loss intervals by the Flynn-Wall method

| Polymer | Mass loss range | E_a | \bar{E}_a |
|-----------|-----------------|----------------------|-------------|
| | | kJ mol ⁻¹ | |
| PDMOEI-40 | | 99.2 | |
| PDMOEI-50 | 10-60 | 100.5 | 103.5 |
| PDMOEI-60 | | 110.9 | |
| PDMOEI-40 | | 108.5 | |
| PDMOEI-50 | 10-90 | 107.7 | 112.5 |
| PDMOEI-60 | | 121.4 | |
| PDEOEI-40 | | 87.5 | |
| PDEOEI-50 | 10-60 | 85.2 | 91.3 |
| PDEOEI-60 | | 101.1 | |
| PDEOEI-40 | | 95.5 | |
| PDEOEI-50 | 10-90 | 94.2 | 97.2 |
| PDEOEI-60 | | 102.0 | |
| PDPOEI-40 | | 94.7 | |
| PDPOEI-50 | 10-60 | 89.4 | 92.5 |
| PDPOEI-60 | | 93.3 | |
| PDPOEI-40 | | 106.1 | |
| PDPOEI-50 | 10-90 | 99.0 | 103.0 |
| PDPOEI-60 | | 104.2 | |
| PDBOEI-40 | | 86.8 | |
| PDBOEI-50 | 10-60 | 94.3 | 89.5 |
| PDBOEI-60 | | 87.4 | |
| PDBOEI-40 | | 93.8 | |
| PDBOEI-50 | 10-90 | 102.8 | 97.7 |
| PDBOEI-60 | | 96.6 | |

the case of poly(di-*n*-alkyl itaconates) (PDAlkyl-I), polymers which also thermally degrade predominantly by depolymerisation, the E_a is independent of molar mass of the polymer over a wide range of molar masses [10, 11]. This has been explained by chain transfer to polymer during thermal depolymerisation which reintroduces thermally weak structures into the degrading polymer [13]. However, in the homologous series of PDAlkyl-I the E_a decreases slightly

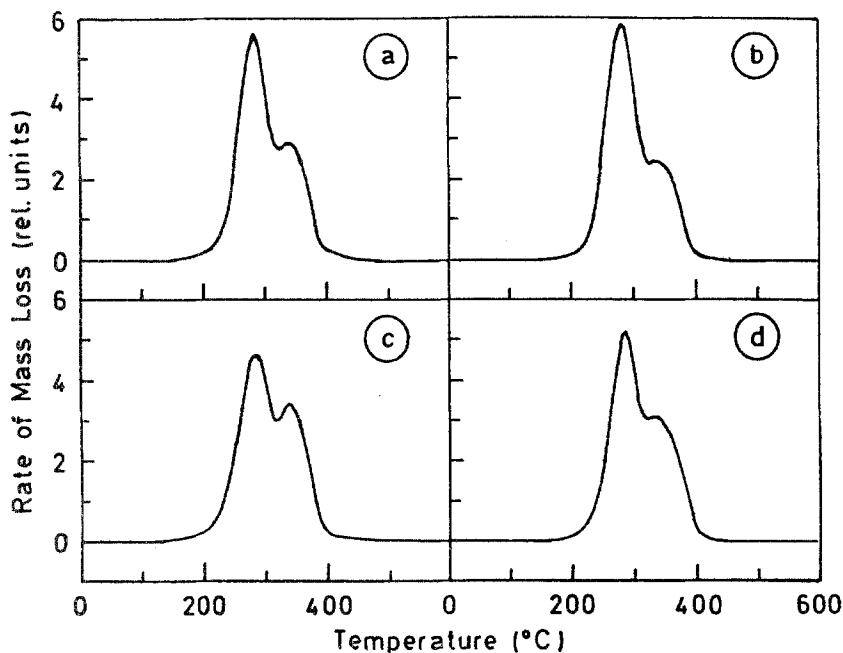


Fig. 2 Non-oxidative DTG curves of poly(dialkoxyethyl itaconates), a) PDMOEI, b) PDEOEI, c) PDPOEI and d) PDBOEI, heating rate $2.5^{\circ}\text{C min}^{-1}$, nitrogen flow rate $22\text{ cm}^3\text{ min}^{-1}$

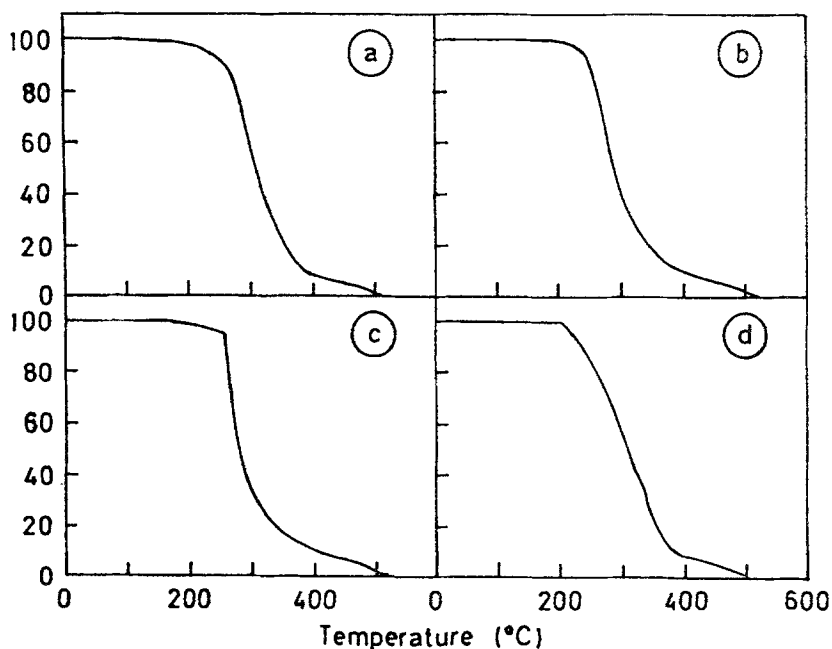
starting from the dimethyl to the di-*n*-octyl ester. In this respect the poly(dialkoxyethyl itaconate) (PDAalkoxy-I) homologous series differs from the PDAalkyl-I homologous series.

The corresponding differential TG (DTG) curves of the PDAalkoxy-I, recorded at a heating rate of $10^{\circ}\text{C min}^{-1}$, are shown in Figs 2a–d. Typical of PDAalkyl-I [11], the two stage mass loss can be clearly seen in these DTG curves. The temperatures of the peak maxima are given in Table 4. What is surprising is the size of the first peak. In the case of PDAalkyl-I the first peak in the DTG curves was assigned to chain end initiated and the second to main chain scission initiated depolymerisation. The relative magnitude of the peaks changed starting from poly(dimethyl itaconate) (PDMI) to poly(di-*n*-octyl itaconate) (PDOI) with the first peak decreasing and the second peak increasing in size with increasing size of the ester substituent. The shape of the DTG curves of the PDAalkoxy-I resembles the DTG curves of the lower members of the PDAalkyl-I homologous series much more than the DTG curves of the higher ones which have two distinct peaks [11].

Preliminary isothermal degradation experiments showed that the respective monomer is present in the degradation products indicating that depolymerisation is a degradation pathway, but the shape of the DTG curves might suggest

Table 4 Positions of the non-oxidative DTG maxima of the investigated polymers, heating rate $2.5^{\circ}\text{C min}^{-1}$, nitrogen flow rate $22\text{ cm}^3\text{ min}^{-1}$

| Polymer | $T_{\text{max}1}/^{\circ}\text{C}$ | $T_{\text{max}2}/^{\circ}\text{C}$ |
|-----------|------------------------------------|------------------------------------|
| PDMOEI-40 | 285.5 | 341.8 |
| PDMOEI-50 | 283.8 | 343.0 |
| PDMOEI-60 | 288.3 | 348.3 |
| PDEOEI-40 | 281.5 | 341.3 |
| PDEOEI-50 | 282.5 | 342.5 |
| PDEOEI-60 | 286.8 | 346.3 |
| PDPOEI-40 | 285.3 | 339.5 |
| PDPOEI-50 | 287.5 | 340.0 |
| PDPOEI-60 | 289.5 | 342.0 |
| PDBOEI-40 | 286.5 | 336.5 |
| PDBOEI-50 | 288.8 | 345.0 |
| PDBOEI-60 | 288.3 | 340.8 |

**Fig. 3** Oxidative TG curves of poly(dialkoxyethyl itaconates), a) PDMOEI, b) PDEOEI, c) PDPOEI and d) PDBOEI, heating rate $10^{\circ}\text{C min}^{-1}$, air flow rate $15\text{ cm}^3\text{ min}^{-1}$

that side chain scission plays an important role in the thermal degradation of these polymers. The detailed non-oxidative thermal degradation mechanism of PDalkoxy-I will be the subject of a separate paper.

If the results concerning the non-oxidative thermal degradation were somewhat unexpected compared to the results of the non-oxidative thermal degradation of PDalkyl-I, the results of the oxidative thermal degradation of the PDalkoxy-I were completely surprising.

Figures 3a-d show the TG curves of the four polymers recorded at a heating rate of $10^{\circ}\text{C min}^{-1}$ and an air flow rate of $15\text{ cm}^3\text{ min}^{-1}$. The curves are all characterised by a very rapid mass loss once the initial decomposition has commenced. This was especially pronounced in the case of PDPOEI. This effect also manifested itself in the DTG curves of the polymers, shown in Figs 4a-d. The mass loss, although very rapid, was not rapid enough to be caused by polymer combustion which results in almost vertical TG curves and DTG curves which are out of the instrument range. This led us to conclude that the rapid mass loss was probably the result of an exothermic process leading to an uncontrolled increase of the sample temperature, with a consequential uncontrolled reaction rate and mass loss. Attempts to control this process by reducing the sample size were not successful as can be seen from Fig. 5, which shows the TG curves recorded with samples of different mass. It can be clearly seen from Fig. 5 that

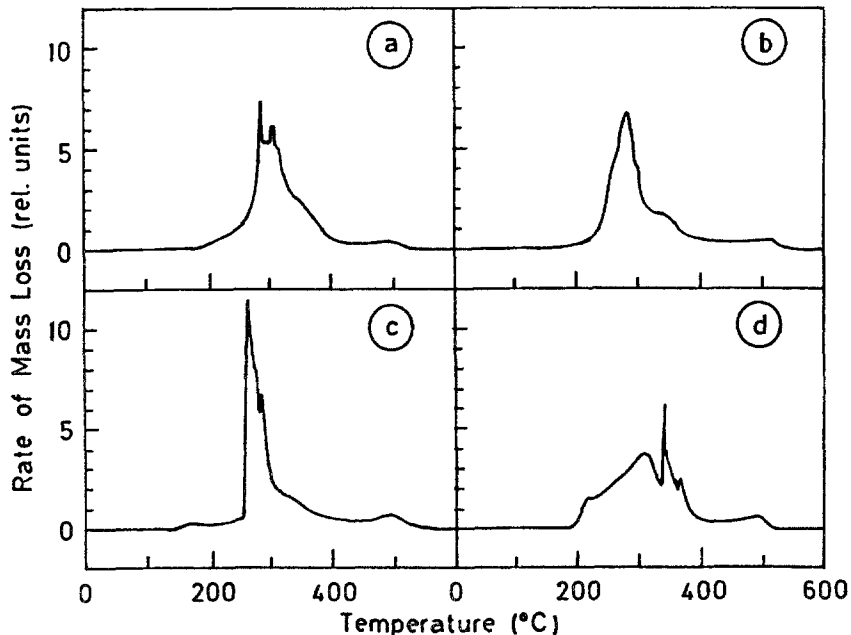


Fig. 4 Oxidative DTG curves of poly(dialkoxyethyl itaconates), a) PDMOEI, b) PDEOEI, c) PDPOEI and d) PDBOEI, heating rate $10^{\circ}\text{C min}^{-1}$, air flow rate $15\text{ cm}^3\text{ min}^{-1}$

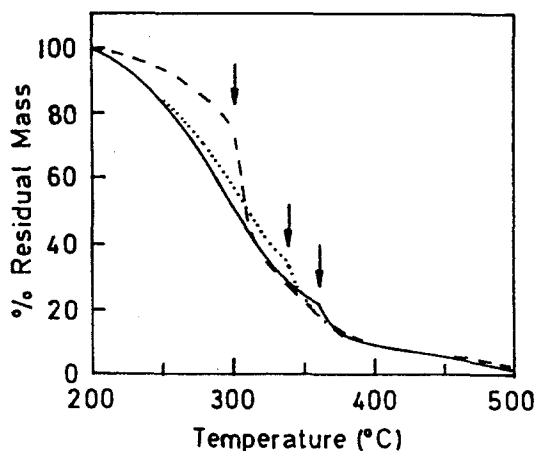


Fig. 5 Oxidative TG curves of PDBOEI-50 using different sample masses, (—) 1.04 mg, (···) 2.85 mg and (---) 5.22 mg, heating rate $10^{\circ}\text{C min}^{-1}$, air flow rate $15\text{ cm}^3\text{ min}^{-1}$

reduction of the sample mass shifts the onset of uncontrolled mass loss to higher temperatures and decreases the size of the effect. This fact again suggests that an exothermic reaction is responsible for the increased rate of mass loss. Because of the rapid uncontrolled mass loss it was impossible to determine meaningful characteristic degradation temperatures as was the case for the non-oxidative thermal degradation of the polymers. Apparent activation energies of mass loss could also not be determined as the onset of rapid mass loss was also heating rate dependent which led to a series of TG curves which crossed over one another.

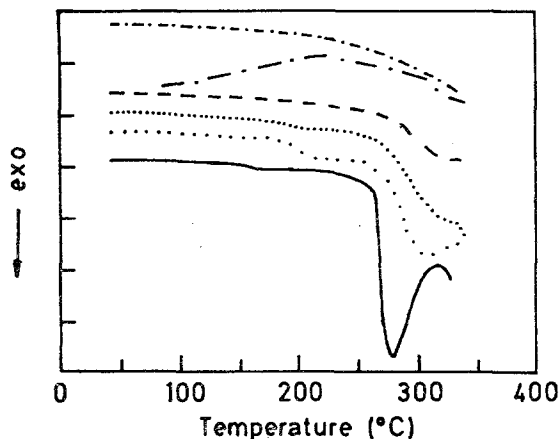


Fig. 6 DSC curves of dialkoxyethyl itaconates, heating rate $10^{\circ}\text{C min}^{-1}$, air flow rate $25\text{ cm}^3\text{ min}^{-1}$, $R = 10\text{ mcal s}^{-1}$, (---) base line, (---) DBI, (- - -) DMOEI, (- · - · -) DEOEI, (—) DPOEI and (· · · ·) DBOEI

One possible exothermic reaction causing such erratic TG curves, could be repolymerisation of the initially formed monomer. In order to investigate this possibility, DSC measurements were performed on each of the monomers as well as di-*n*-butyl itaconate (DBI). The curves resulting from these measurements are shown in Fig. 6. These curves confirm that exothermic reactions do occur when the dialkoxyethyl itaconate monomers are heated in air. The heat released can not be calculated as the exothermic reactions are accompanied by considerable mass loss. However, it can be seen from Fig. 6 that DPOEI shows the largest exothermal effect. In the oxidative TG analysis PDPOEI had the steepest mass loss and the most irregular DTG curve.

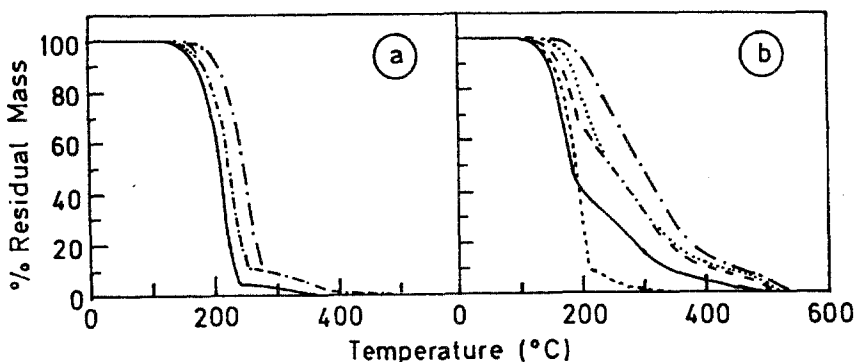


Fig. 7 a) Non-oxidative and b) oxidative TG curves of dialkoxyethyl itaconates, (—) DMOEI, (----) DEOEI, (· · · ·) DPOEI, (-·-·-) DBOEI and (- - -) DBI, heating rate $10^{\circ}\text{C min}^{-1}$, nitrogen flow rate $22\text{ cm}^3\text{ min}^{-1}$, air flow rate $15\text{ cm}^3\text{ min}^{-1}$

Oxidative and non-oxidative TG analysis of the four monomers was also performed. Figure 7a shows the non-oxidative TG curves for the four alkoxyethyl itaconate monomers, while the oxidative TG curves are presented in Fig. 7b, as well as the curve for DBI for comparison. The non-oxidative curves, Fig. 7a, simply represent loss of monomer by evaporation, the different curves reflecting the boiling point of the respective monomers. The oxidative TG curves are much more complex. The TG curve of DBI is simple, again representing only evaporation, whereas the curves for the dialkoxyethyl itaconates, after initial mass loss due to evaporation, indicate that thermally more stable compounds are formed. In the case of DMOEI approximately 60% of the mass loss is due to monomer evaporation, whereas only about 40% is due to boiling in the cases of DEOEI, DBOEI and DPOEI.

This supports the hypothesis that, during the oxidative thermal degradation of PDAlkoxy-I, the monomer formed in the initial stages of degradation is subjected to repolymerisation. When the DTG curves of the oxidative thermal degradation of the monomers are compared to the corresponding curves of the polymer (Figs 8a-d) this hypothesis gains further in weight as the degradation

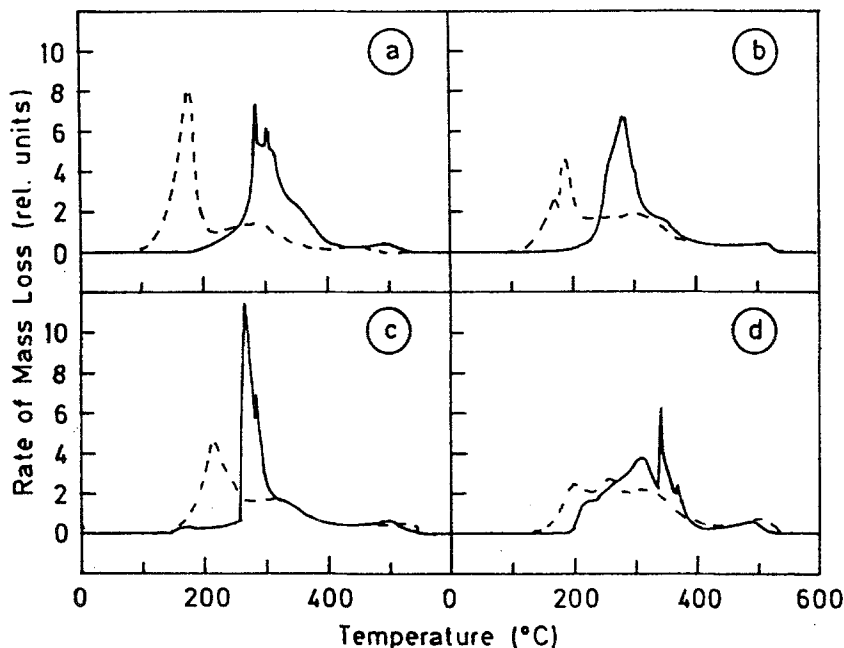


Fig. 8 Oxidative DTG curves of a) PDMOEI and DMOEI, b) PDEOEI and DEOEI, c) PDPOEI and DPOEI and d) PDBOEI and DBOEI, (—) polymer, (---) monomer, heating rate $10^{\circ}\text{C min}^{-1}$, air flow rate $15\text{ cm}^3\text{ min}^{-1}$

of the residue left after evaporation clearly shows a DTG curve which corresponds to the curves resulting from the oxidative degradation of the respective polymers.

It is proposed that during the thermal degradation of PDAlkoxy-I a considerable amount of side chain scission occurs as a result of the relatively thermally labile C–O bonds. This would explain the large first DTG peak observed during the non-oxidative thermal degradation of these polymers. The radicals formed could react with oxygen leading to peroxy radicals which could then initiate the repolymerisation of the monomer formed during thermal depolymerisation. The extremely large effect with the di-*iso*-propoxy ester most likely reflects the increased stability of the isopropoxy radical, a secondary carbon radical, and/or the increased reactivity of the isopropoxy peroxy radical to polymerisation initiation.

The exact reaction routes of radical formation cannot be given at the moment, but oxygen must be involved or a similar repolymerisation process would occur in the non-oxidative degradation with an accompanying exothermic reaction. It is hoped, however, that the results of product analysis will enable the elucidation of the mechanism of polymerisation initiation in an oxidative atmosphere.

The occurrence of repolymerisation at the elevated temperatures implies that the ceiling temperatures for poly(dialkoxyethyl itaconates) must be high. Theoretical calculations [21] indicate that it is possible that poly(itaconates) have high ceiling temperatures [22]. These predictions would need to be confirmed by experimental evidence.

References

- 1 C. S. Marvel and T. H. Shepherd, *J. Am. Chem. Soc.*, **24** (1959) 599.
- 2 S. Nagai and K. Yoshida, *Kobunshi Kagaku*, **17** (1960) 79; *Chem. Abst.* **55** (1960) 14973g.
- 3 B. E. Tate, *Adv. Polym. Sci.*, **5** (1967) 214.
- 4 J. M. G. Cowie, *Pure Appl. Chem.*, **51** (1979) 2331 and refs. cited therein.
- 5 J. Veličković and S. Vasović, *Makromol. Chem.*, **153** (1972) 207.
- 6 J. Veličković, V. Juraničova and J. Filipović, *Angew. Makromol. Chem.*, **24** (1972) 77.
- 7 J. Veličković and J. Filipović, *Polym. Bull.*, **5** (1981) 569.
- 8 J. M. G. Cowie and Z. Haq, *Brit. Polym. J.*, (1977) 246.
- 9 J. Veličković and I. Popović, *Croat. Chem. Acta*, **60** (1987) 173, *Chem. Abstr.*, **107** (1987) 59599h.
- 10 I. G. Popović, *Thermochim. Acta*, **134** (1988) 127.
- 11 I. G. Popović, L. Katsikas and J. S. Veličković, *J. Thermal Anal.*, **38** (1992) 953.
- 12 I. G. Popović, L. Katsikas, K. A. Voloshchuk, S. Schrötter and J. S. Veličković, *Polym. Deg. Stab.*, **42** (1993) 345.
- 13 I. G. Popović, L. Katsikas, H. Weller, S. Schrötter and J. S. Veličković, *J. Appl. Polym. Sci.*, **50** (1993) 1475.
- 14 J. M. G. Cowie and R. Ferguson, *J. Polym. Sci., Polym. Phys. Edn.*, **23** (1985) 2181.
- 15 J. M. G. Cowie and A. C. S. Martin, *Polym. Commun.*, **26** (1985) 298.
- 16 B. K. Coltrain, W. T. Ferrar and J. M. Salva, *J. Polym. Sci., Polym. Chem. Edn.*, **31** (1993) 2261.
- 17 I. A. Katime, F. Palomares, L. C. Cesteros, C. Laborra and E. Dominguez, *Thermochim. Acta*, **142** (1989) 317.
- 18 N. Stanojević, L. Katsikas, D. M. Petrović-Djakov, J. M. Filipović, J. S. Veličković and I. G. Popović, *Eur. Polym. J.*, **31** (1995) 541.
- 19 J. H. Flynn and L. A. Wall, *Polym. Letts.*, **4** (1966) 323.
- 20 N. Grassie, E. Vance, *Trans. Faraday Soc.*, **49** (1953) 184.
- 21 D. W. van Krevelen, 'Properties and Chemical Structure of Polymers' (Russian translation), Himiya, Moscow 1976.
- 22 The calculation yields the same T_c value for poly(itaconic acid) and all its diesters, 316°C, because the contributions of the two identical ester substituents cancel one another out.