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AUTHORS' REVIEW

The thermal degradation of some polymeric di-alkyl esters of itaconic acid[•]

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Abstract: One group of polymers that may help relieve the dependence on crude oil is based on itaconic acid, the biotechnological production of which has become feasible. Itaconic acid and its derivatives can easily be incurporated into polymers and may serve as a substitute for petrochemically derived acrylate or methacrylate monomers. The applications of polymers based on itaconic di-esters depend largely on their thermal stability. The thermal stability of poly(di-itaconates) is dependent, not only on the general structure of the monomer repeating unit, but also on the structure of the ester substituent. Depolymerization, initiated by β-scission or random main chain scission, is the dominant thermolysis mechanism in most cases. The deploymerization of poly-(di-itaconates) may be accompanied by de-esterification, elimination, cross-linking, random main or side chain scission and carbonization. Comparison of the thermal degradation mechanism of polymeric di-esters of itaconic acid to that of corresponding poly(methacrylates) confirms the viability of substituting poly(methacrylates) by poly(di-itaconates).

Keywords: itaconic acid; polyitaconates; thermal degradation; biosynthetic polymers.

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1. INTRODUCTION

The role of plastics in modern society is being re-examined due to problems related to the persistence of mass polymers in the environment. Plastics, considered as the marvel of modern society, have replaced traditional materials such as wood, cotton, wool, stone, metal, glass or ceramics in many of their former uses and feature in advanced technologies from engineering materials to high tech applications. On the negative side, plastics deteriorate, but do not decompose under ambient conditions. Some plastics can and are being recycled, but mostly they are disposed of in landfills, incinerated or used to produce electricity at waste-to-energy plants, all of which have their downsides, especially concerning environmental pollution.[1] Moreover, plastic debris is found in water bodies, in oceans[2,3] and freshwater lakes,[4] enabling them to enter the human food chain *via* filter feeders.

Nevertheless, life without plastics is hardly imaginable. Plastics consist mainly of synthetic polymers, predominantly based on petrochemicals. As crude oil reserves diminish and oil prices inevitably increase due to ever increasing global needs, as far as polymers are concerned, a more sustainable approach for polymer scientists could be to search for biosynthetic polymers that can match the performance of synthetic ones.

One group of polymers that may help relieve the dependence on crude oil, is based on itaconic acid (methylene succinic acid, 2-methylidenebutanedioic acid (IUPAC)). Itaconic acid (IA) is an unsaturated dicarbonic organic acid. IA and its derivatives can easily be incorporated into polymers and may serve as a substitute for traditional acrylate and methacrylate monomers.

The biosynthesis of itaconic acid by fermentation processes has been known for a long time.[5] The price, however, has not been competitive in comparison to the IA obtained by petrochemical means. This aspect has now changed. More than 80,000 tons of IA are produced worldwide annually and sold at a price of around US\$ 2/kg.[6] In time, biosynthetic polymers based on IA could become attractive alternatives to acrylics. The most common representatives of the di-alkyl itaconates, the methyl and ethyl di-esters of IA, can be synthesized by esterifying with biomethanol[7] or bioethanol.[8]

Dibasic IA is a building block that enables the synthesis of monomers for homo-, co- and terpolymers that are structurally more diverse than poly(methacrylates). It is possible to make di-esters, mono-esters and mixed esters with various substituents, as well as di-amides, amino acids and imides.

IA derivatives are widely used or are being investigated as co-components in various formulations in controlled drug release systems,[9,10] for paints and coatings,[11,12] in resist compositions,[13] for contact lenses[14] and ocular lenses[15] and personal care compositions.[16]

The applications of polymers based on itaconic di-esters most commonly depend on their mechanical properties and thermal stability. This review will focus on the thermal degradation behaviour of poly(di-itaconates) and compare it with the thermolysis of polymethacrylates.

2. POLY(DIMETHYL ITACONATE) (PDMI) *vs.* POLY(METHYL METHACRYLATE) (PMMA)

Very early in the study of methacylate polymers, Grassie[17] showed that the thermal degradation of PMMA proceeded almost completely by depolymerization, the yield of monomer being about 99 %. Thermogravimetric (TG) investigations, however, showed that the thermal degradation of PMMA occurred in three stages, as demonstrated by the differential TG (DTG) curves shown in Fig. 1,[18] all of which represented depolymerization of the polymer. PMMA deploymerization was first initiated by the scission of head-to-head bonds in the polymer, followed by β-scission at the vinylidene chain ends and, finally, by random main chain scission. Head-to-head bonds and chain-end unsaturation may be eliminated by changing the conditions of synthesizing PMMA. A thermally more stable PMMA is obtained by radical polymerization in the presence of chain-transfer agents or anionic polymerization.
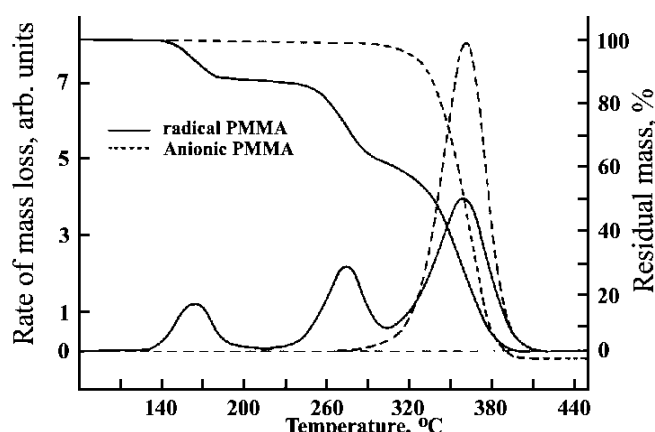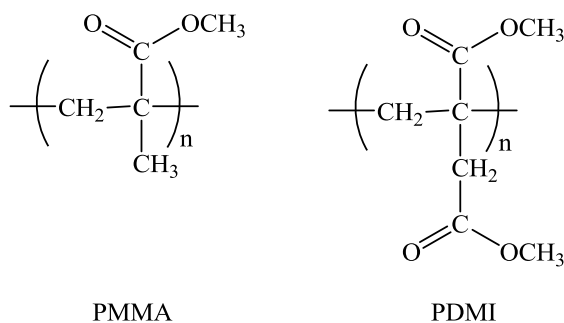

Fig. 1. Effects of the polymerization method on DTG curves for PMMA samples degrading in nitrogen: radically polymerized (——) and anionically polymerized (-----).[18]

The structures of the repeating units of PMMA and PDMI are:

PMMA   PDMI

Analysis of the volatile products of PDMI thermal degradation showed that dimethyl itaconate (DMI) monomer was the main product, about 95 %.[19,20] Very small amounts of methane, carbon dioxide and carbon monoxide are evolved during the thermolysis of PDMI, as seen in Fig. 2. The DTG curves are expected to be similar to those of PMMA. However, as seen in Fig. 3, there are only two DTG maxima, corresponding to the second and third peak of the PMMA DTG curve. This difference may be explained by the structure of the itaconate monomer. No head-to-head bonds are formed during di-itaconate bulk radical polymerization because of steric hindrance to the approach of two bulky propagating radicals. Nagai and Yoshida[21] proposed that, due to the allylic structure of the di-itaconate monomers, chain transfer to monomer would be favoured during radical polymerization. This hypothesis was later confirmed by us.[22–24] Thus, PDMI
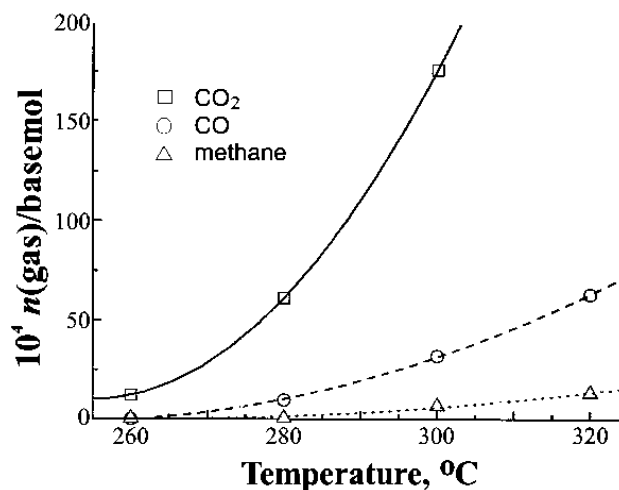

Fig. 2. The amount of CO_2 (□), CO (○) and methane (Δ) formed during the thermal degradation of PDMI as a function of temperature, heating time 30 min.[20]

depolymerization is initiated by β-scission at chain-end unsaturation and, at higher temperatures, by random main chain scission. The double bonds at the chain ends originate not only from termination by disproportionation, but also from considerable chain-transfer to monomer during radical polymerization. As PDMI does not have any β-hydrogens in the ester substituents, no relevant ester decomposition is expected. Very small amounts of methanol were detected in the thermolysis volatiles.[20]
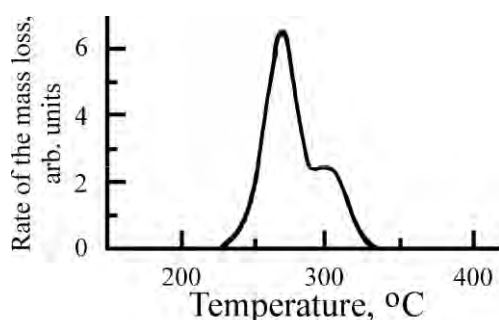

Fig. 3. The DTG curve of PDMI, heating rate: 2.5 °C min^{-1}, nitrogen flow rate: 25 cm[3] min^{-1}.[19]

The depolymerization of PDMI is accompanied by a decrease in polymer molar mass, Fig. 4a. It is useful to analyse the decrease in relative molar mass as a function of conversion, *i.e.*, mass loss, Fig. 4b. The shape of the curve indicates that the kinetic chain length of depolymerization, *Z*, is low. *Z* is derived from the following equation:[25]

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

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 polymerization of the initial and degraded polymer, respectively. This calculation does not consider chain transfer reactions, only depropagation. The values of *Z* for PMMA range between 1000 and 2000 in the temperature range 260–300 °C,[25] while the values of *Z* for PDMI in the same temperature interval are no greater than 20.[26] The low value of Z implies that chain transfer to polymer occurs during the dezipping process and that, in this case, *Z* may only be considered as an apparent value.

3. POLY(DI-*n*-ALKYL ITACONATES)

*3.1. Thermal degradation of poly(di-*n*-alkyl itaconates) polymerized in bulk*

The general structures of poly(methacrylates) and poly(di-itaconates) are:

Poly(methacrylate)   Poly(di-itaconate)
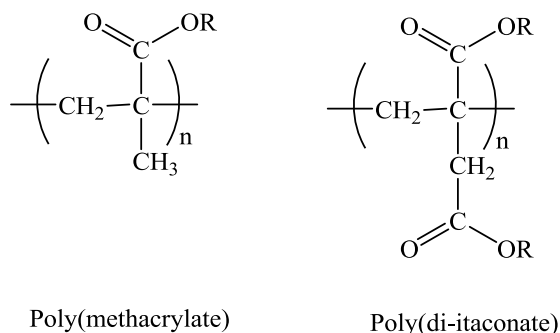
As the *n*-alkyl substituent in poly(di-itaconates) increases in length, deploy-merization remains the dominant thermal degradation mechanism with monomer yields ranging from 85 to 90 %. The appearance of *β*-hydrogens in the ester sub-stituent allows for the occurrence of ester decomposition during thermolysis. Poly(di-*n*-alkyl itaconates) have two *β*-hydrogens, except poly(di-ethyl itaconate)
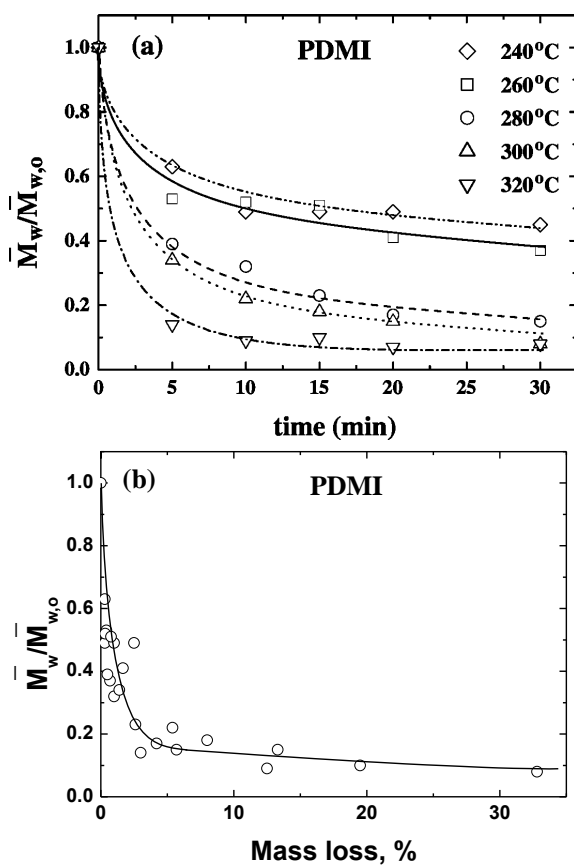
Fig. 4. Changes in the relative molar mass of PDMI as a) a function of time at various degradation tempe-ratures and b) a function of mass loss at various times and tempe-ratures.[19]

(PDEI), which has three. The role of β-hydrogens in the thermal degradation of poly(methacrylates) is well documented.[27] Ester decomposition leads to the evolution of 1-alkenes and to the formation of free acid groups in the polymer chain according to the following mechanism (Scheme 1).
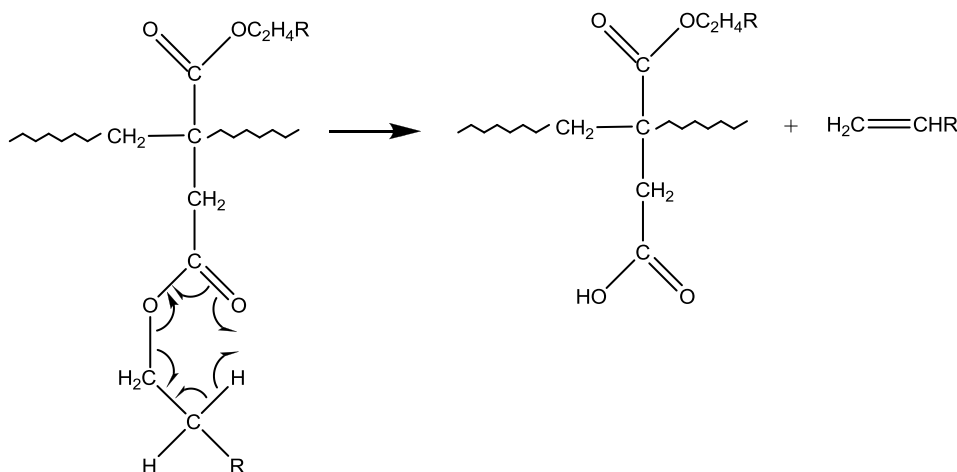
Scheme 1. Ester decomposition.[20]

Most of the other detected degradation products such as the corresponding *n*-alkanols, *n*-alkyl acetates, *n*-alkyl acrylates, *n*-alkyl methacrylates, *n*-alkyl esters of 3-methylene butyric acid, corresponding isomeric mesaconates and citraconates and di-*n*-alkyl esters of 1-methyl succinic acid, may be related to processes initiating depolymerization. The possible scission sites are shown below (Scheme 2).
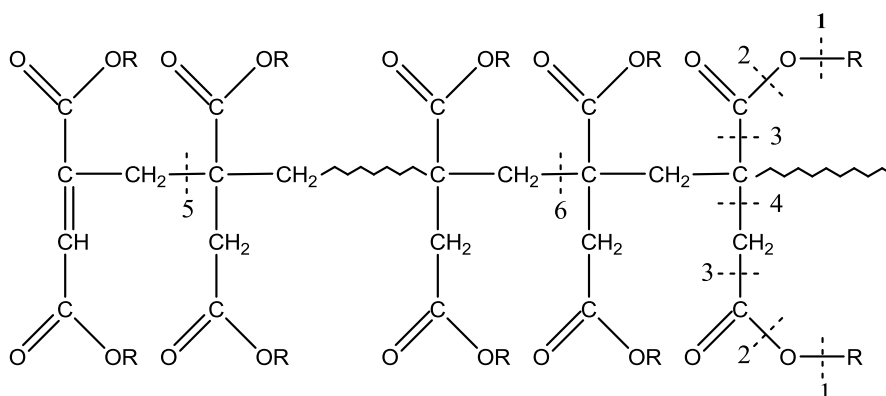
Scheme 2. Possible scission sites.[20]

The amounts of evolved carbon dioxide and carbon monoxide as a function of substituent size do not vary much. In the case of PDEI, ester decomposition is preferred to CO_2 and CO evolution, Fig. 5.
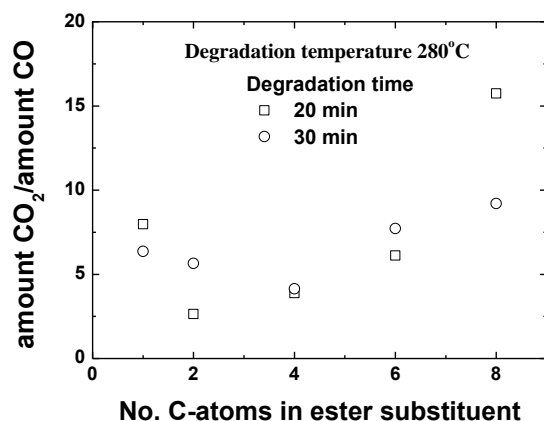

Fig. 5. The ratio of the amount of CO_2 and CO evolved as a function of number of carbon atoms in the ester substituent at various temperatures, degradation time 30 min.[20]

The availability of chain-end double bonds in poly(di-*n*-alkyl itaconates) decreases as the length of the substituent increases. As the substituents become bulkier, chain transfer to monomer is suppressed during polymerization due to steric hindrance. Consequently, depolymerization is still initiated by chain-end *β*-scission and random main chain scission, the chain end structures originating from termination by disproportionation. The DTG curves of some poly(di-*n*-alkyl itaconates) are shown in Fig. 6.[28]
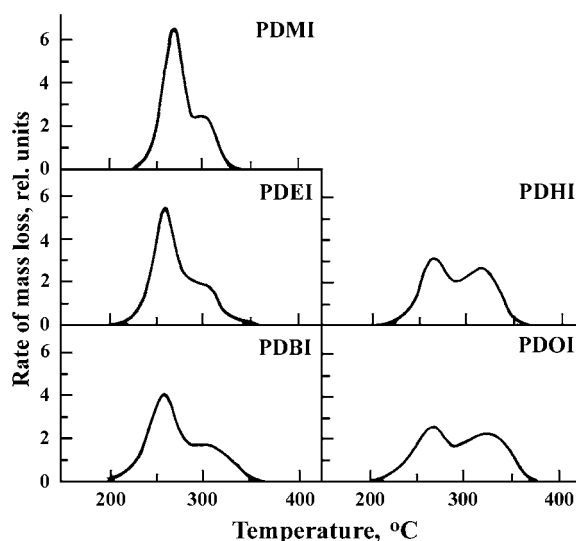

Fig. 6. The DTG curves of PDMI, PDEI, PDBI, PDHI and PDOI, heating rate 2.5 °C min^{-1}, nitrogen flow rate 25 cm[3] min^{-1}.[28]

The higher poly(di-*n*-alkyl itaconates), starting from poly(di-*n*-butyl itaconate) (PDnBI), tend to branch and crosslink at lower degradation temperatures, $t < 280$ °C, Fig. 7. In the case of poly(di-*n*-octyl itaconate) (PDOI), some insoluble swellable gel is formed. The possibility of hydrogen abstraction increases as the *n*-alkyl substituent becomes longer, so radical–radical combination may lead to branching and even crosslinking. As the degradation temperature and time increase, chain scission predominates and the polymer molar mass decreases. The kinetic chain lengths of depropagation are low for all the poly(di-*n*-alkyl itaconates) and the Z values are not higher than 20, Fig. 8. The changes in polymer relative molar mass as a function of polymer mass loss are similar to those for PDMI, indicating that chain transfer to polymer occurs during the depolymerization of poly(di-*n*-alkyl itaconates). A mechanism for the chain transfer reaction is given in the scheme below (Scheme 3).[28]
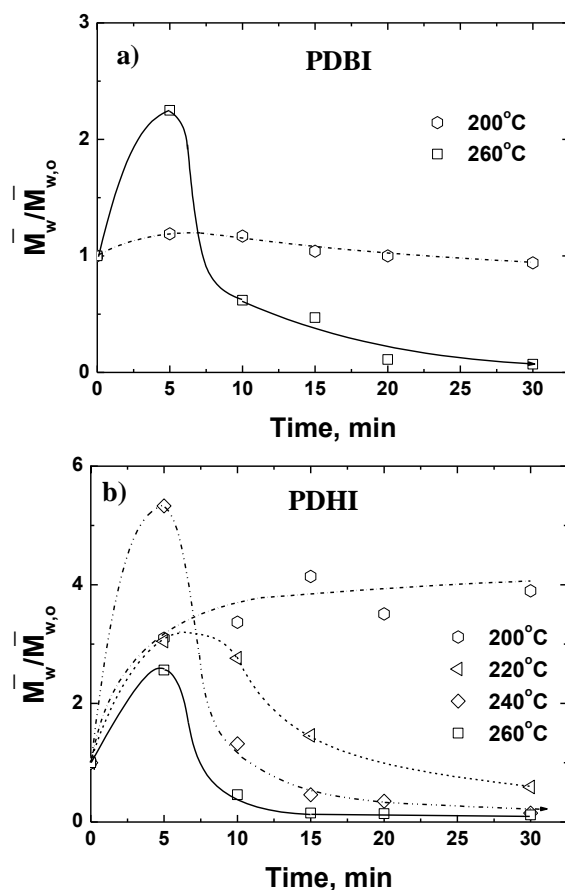

Fig. 7. Changes in the relative molar masses of the degraded polymer residues of a) PDnBI and b) PDHI as a function of degradation temperature and time.[28]
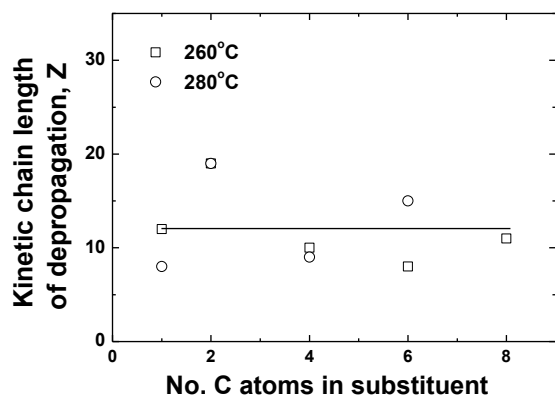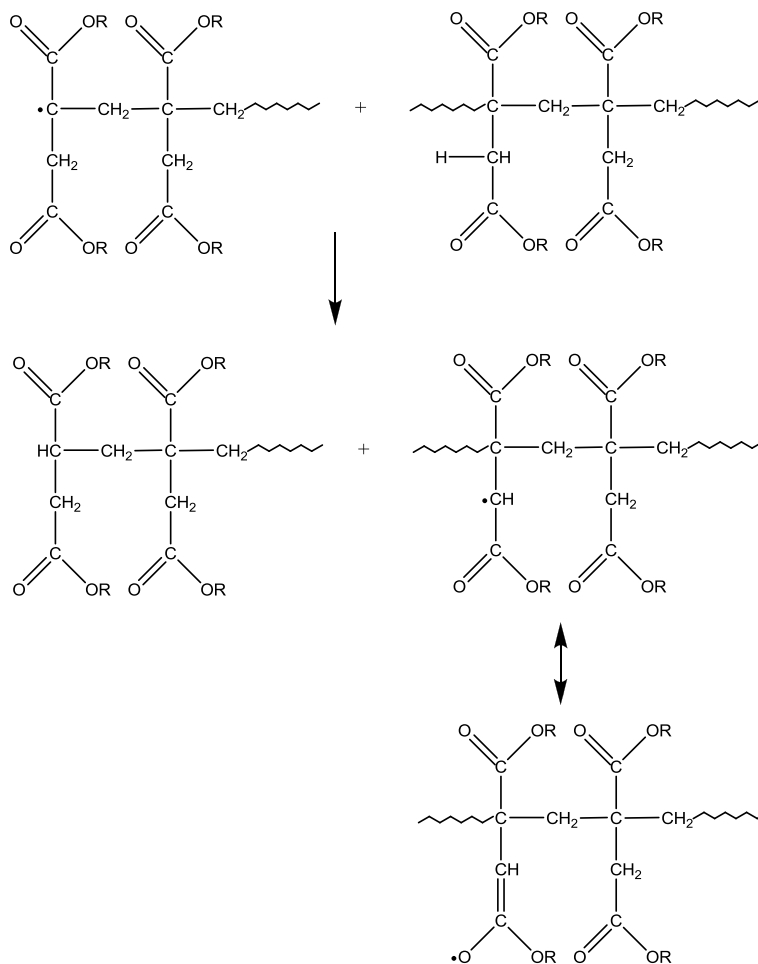
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Fig. 8. Kinetic chain length of depropagation for poly(di-n-alkyl itaconates) as a function of the size of the alkyl substituent, degradation temperature 260 (□) and 280 °C (○), degradation time 30 min.[28]

Scheme 3. Chain transfer to polymer.[28]

The number of main chain scissions per monomer unit can serve as a useful measure of polymer thermal stability. The value of s/P_0 may be calculated from the following equation:

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

where s is the number of scissions and x is the fraction of evaporated thermolysis volatiles. As expected, the values of s/P_0 increase with increasing degradation temperature and exposure time. Poly(di-n-hexyl itaconate) (PDHI) was chosen as an example to show this trend, Fig. 9. The thermal stability of poly(di-n-alkyl itaconates) decreases with increasing length of the n-alkyl substituent, Fig. 10.[28]
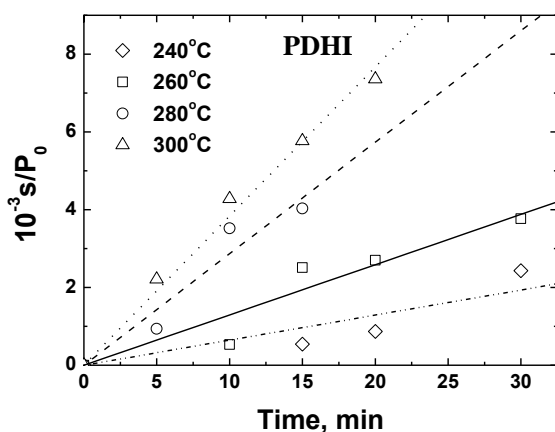

Fig. 9. Number of bonds broken per monomer unit during the thermal degradation of PDHI at various temperatures as a function of time.[28]
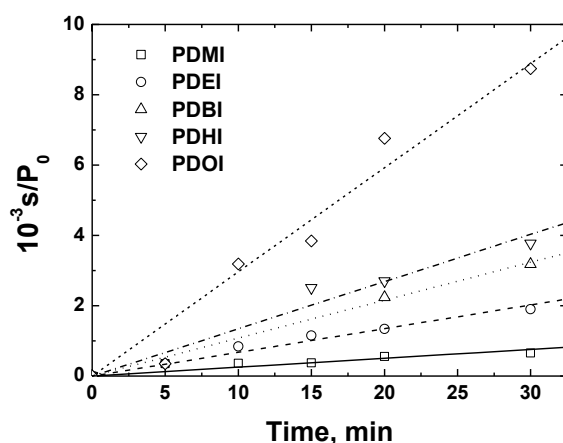

Fig. 10. Number of bonds broken per monomer unit during the thermal degradation of poly(di-n-alkyl itaconates) at 260 °C as a function of time.[28]

3.2. Thermal degradation of poly(di-n-alkyl itaconates) polymerized in bulk in the presence of chain transfer agents

The thermal stability of poly(di-*n*-alkyl itaconates) may be improved by reducing the number of polymer chains with terminal double bonds during polymer synthesis. The thermal degradation of PDHI samples synthesized in the presence of various amounts of *n*-dodecyl mercaptan (DDM) illustrates the phenomenon well.[22] As the growth of polymer chains is terminated by transfer reactions to the thiol, the number of macromolecules with saturated chain-ends increases. The polymer samples are thermally more stable because thermal degradation is initiated predominantly by random main chain scission. The TG and DTG curves of the PDHI samples are shown in Fig. 11.
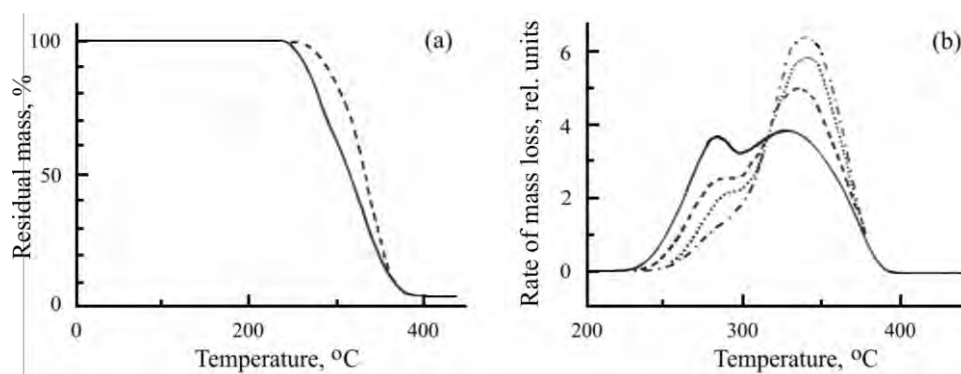

Fig. 11. a) TG curves of PDHI polymerized in the absence (———) and in the presence of 150 mmol L^{-1} of DDM (-----); b) DTG curves of PDHI polymerized in the presence of no (———), 45 (-----), 80 (·······) and 150 (- · - ·) mmol L^{-1} of DDM. Heating rate 10 °C min^{-1}; nitrogen flow rate 25 cm^3 min^{-1}.[22]

3.3. Thermal degradation of poly(di-n-alkyl itaconates) polymerized in solution

As already stated, the thermal stability of poly(di-*n*-alkyl itaconates) depends on the amount of chain-end double bonds present in the polymer sample. Besides standard termination by disproportionation, terminal double bonds are also formed readily by chain transfer to monomer. It is possible to suppress double bond formation by chain transfer agents other than mercaptans. Polymerizations of di-alkyl itaconates have been carried out in various solvents (toluene, chloroform or dioxane).[23,28] In all cases it was possible to significantly decrease the number of formed chain-end double bonds in the polymer, even in benzene, an "inert" solvent with a low tendency to transfer to solvent. Such effective chain transfer by numerous solvents may be explained in the following way.[24,29] The propagation rate constants, k_p, of itaconates are an order of magnitude lower than those of the corresponding methacrylates.[29] Thus, the values of any constant of chain transfer to solvent, $C_S = k_{tr,S}/k_p$, for itaconates, even though the values of

the transfer rates to solvent, $k_{tr,S}$, may be very low, are unusually high. An example is shown in Fig. 12, indicating effective chain transfer to benzene, yielding thermally more stable PDBI samples. The DTG curves clearly demonstrate that the number of unsaturated polymer chain ends decreases when the radical polymerization is performed at higher benzene concentrations.
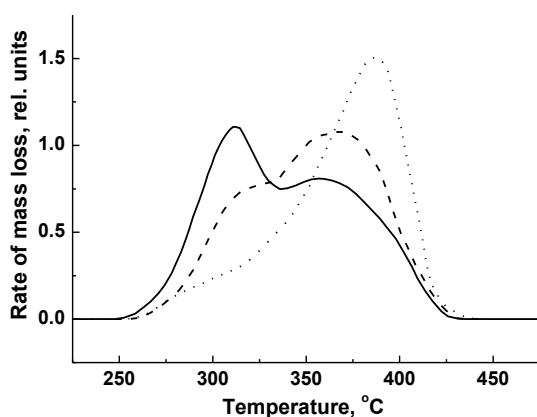

Fig. 12. DTG Curves of PDBI samples synthesized in benzene under nitrogen at 57 °C, 0 (——), 7.78 (-----) and 9.53 (·······) mol dm^{-3} benzene; heating rate: 10 °C min^{-1}; nitrogen flow rate: 25 cm^3 min^{-1}.[23]

4. POLYMERIC DIESTERS OF ISOMERIC DI-ALKYL ITACONATES

The thermal degradation mechanism of poly(di-alkyl itaconates) with isomeric ester substituents becomes more complex. The number of β-hydrogens in the ester substituent determines the susceptibility to ester decomposition. Similar trends have already been observed in the case of poly(methacrylates).[27] Generally, when the number of β-hydrogens is higher than three, de-esterification becomes a major thermolysis pathway. The characteristic TG curves of poly(di-iso-propyl itaconate) (PDiPI), poly(di-sec-butyl itaconate) (PDsBI) and poly(di-iso-butyl itaconate) (PDiBI), having three, five and one β-hydrogen, respectively, are presented in Fig. 13.[30] Characteristic DTG curves of the same polymers are shown in Fig. 14.

The thermal stability of PDiPI and PDsBI differs to that of the poly(di--itaconates) discussed so far. Even though the major thermolysis product in all cases is the respective monomer, the reactions initiating depolymerization differ. The first DTG peak is correlated to monomer being evolved as a consequence of chain-end β-scission. The second DTG peak is assigned to the evolution of monomer initiated by ester decomposition and main chain scission. Carbonaceous residues at 600 °C of about 10 % were found in both cases. The occurrence of ester decomposition during the thermal degradation of PDiPI was confirmed when free acid groups were detected in the degradation residue, Fig. 15, and by the evolution of 1-propene, Fig. 16. The free acid groups are not thermally stable and easily carboxylate leading to the evolution of CO_2, Fig. 16, and the gradual formation of a carbonaceous residue.
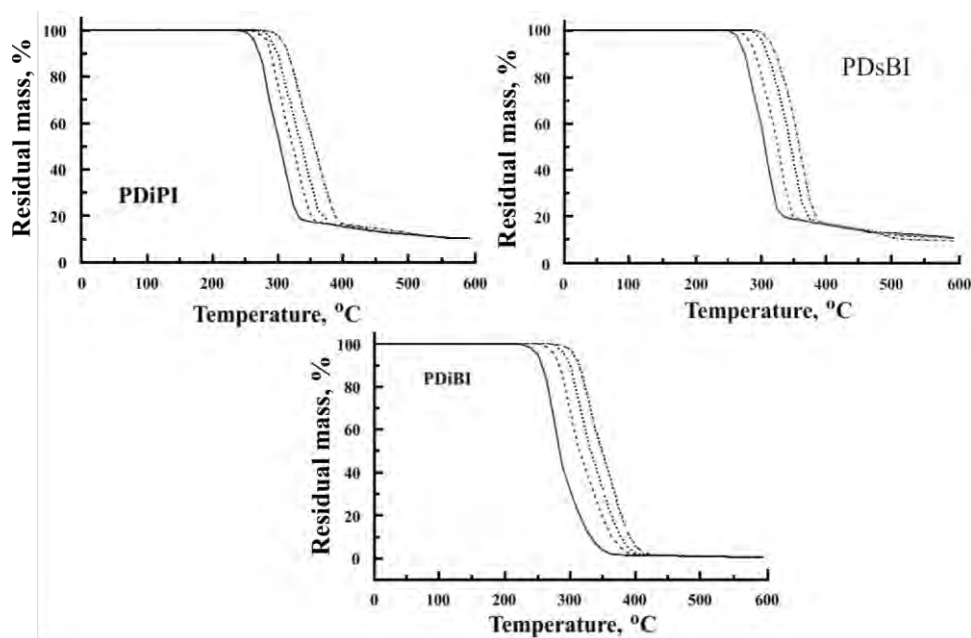
Fig. 13. Non-isothermal TG curves of PDiPI, PDsBI and PDiBI. Heating rates 2.5 (——),
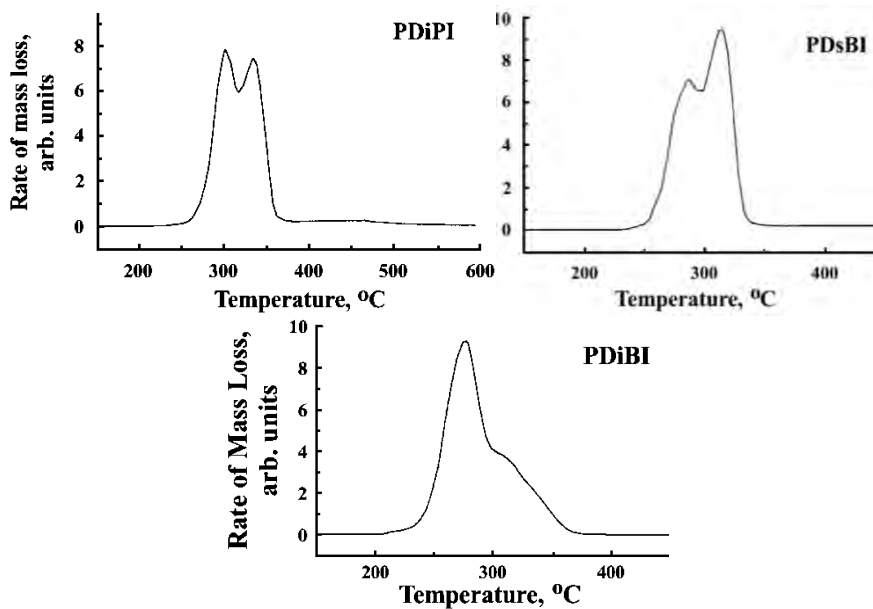10 (-----), 20 (·······) and 40 °C min^{-1} (- · - ·). Nitrogen flow rate: 26 cm^3 min^{-1}.[30]

Fig. 14. Non-isothermal DTG curves of PDiPI, PDsBI and PDiBI. Heating rate: 10 °C min^{-1}.
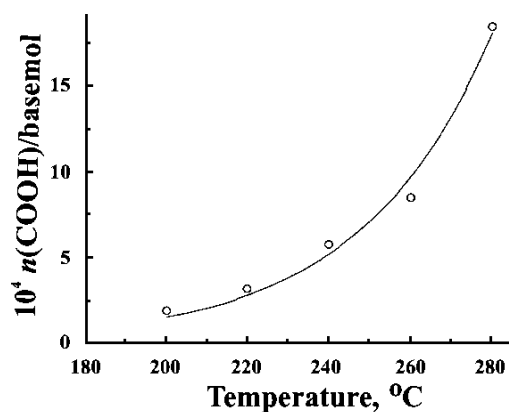Nitrogen flow rate: 26 cm^3 min^{-1}.[30]

Fig. 15. Moles of COOH groups in PDiPI residue as a function of thermolysis temperature, degradation time 30 min.[31]
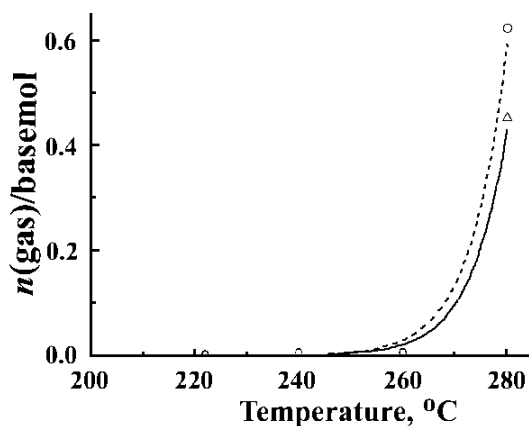
Fig. 16. Moles of evolved CO2 (○) and propene (Δ) per basemol PDiPI as a function of thermolysis temperature, degradation time 30 min.[31]

A similar trend was found in the case of PDsBI. Ester decomposition is extensive, as may be seen in Fig. 17, expressed as butene evolution. It is interesting to compare the thermolysis of PDsBI and its analogue, poly(*sec*-butyl

Fig. 17. Amount of butene evolved on heating PDnBI and PDsBI for 30 min at various temperatures.[32]

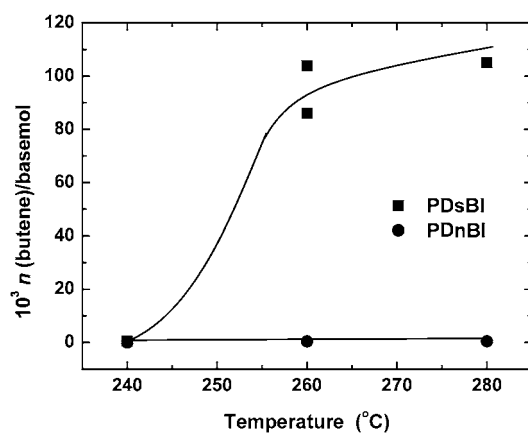methacrylate) (PsBMA).[33] It was established that the thermolysis mechanisms were very similar. Comparable results of free acid group formation in the residue and butene evolution, taking into account the number of ester groups in the monomer unit, were obtained.

PDiBI, with one β-hydrogen in the ester substituent, was found to have similar thermal stability to PDnBI. Depolymerization is the predominant thermolysis mechanism, ester decomposition is almost negligible and there is no carbonization.

5. POLY(DI-ALKOXYETHYL ITACONATES)

The thermal degradation of a series of poly(di-alkoxyethyl itaconates) was investigated: poly(di-methoxyethyl itaconate) (PDMOEI), poly(di-ethoxyethyl itaconate) (PDEOEI), poly(di-propoxyethyl itaconate) (PDPOEI) and poly(di-butoxyethyl itaconate) (PDBOEI). The ester substituents of the four polymers are bulky and they all have two β-hydrogens. Monomer was again the main thermolysis product.[34] The non-isothermal TG curves of these polymers are presented in Fig. 18, while characteristic DTG curves are shown in Fig. 19. The shapes of the DTG curves do not change with substituent size and are similar to those of the lower poly(di-n-alkyl itaconates). However, in this series of polymers, a carbon atom has been substituted by a hetero atom in the substituent, making it thermally less stable due to the presence of C–O bonds. Less energy is required to break these bonds and it is assumed that bond scissions in the substituent efficiently initiate depolymerization. Even though side chain scission is extensive, carbonization does not occur.
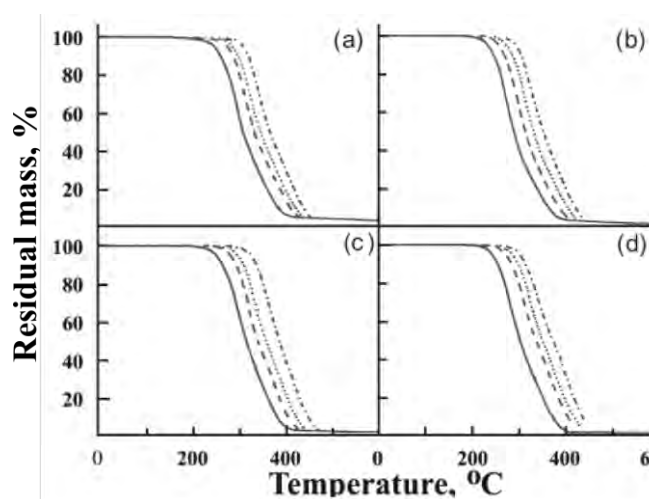

Fig. 18. Non-oxidative TG curves of poly(di-alkoxyethyl itaconates), a) PDMOEI, b) PDEOEI, c) PDPOEI and d) PDBOEI. Heating rates: 2.5 (——), 10 (-----), 20 (······) and 40 °C min^{-1} (- · - ·). Nitrogen flow rate: 22 cm[3] min^{-1}.[32]
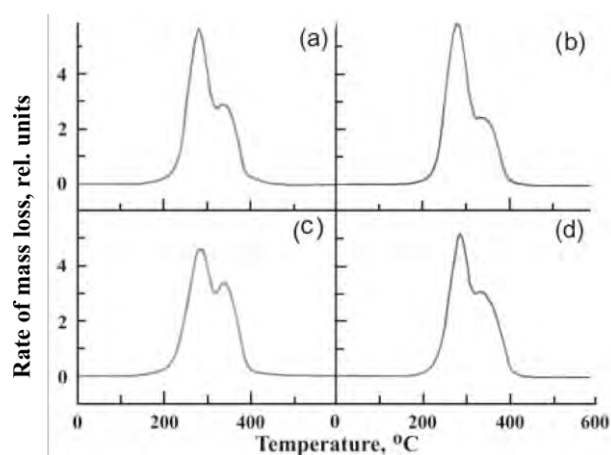
Figure 19. Non-oxidative DTG curves of poly(di-alkoxyethyl itaconates), a) PDMOEI, b) PDEOEI, c) PDPOEI and d) PDBOEI. Heating rate: 10 °C/min (——); nitrogen flow rate: 22 cm^3 min^{-1}.[32]

6. POLY(DI-ALKYLCYCLOHEXYL ITACONATES)

The non-isothermal TG curves of poly(di-cyclohexyl itaconate) (PDCHI), poly(dimethylcyclohexyl itaconate) (PDMCHI) and poly(di-ethylcyclohexyl itaconate) (PDECHI) are presented in Fig. 20, while characteristic DTG curves of these polymers are shown in Fig. 21.[35] There is a clear difference between the TG and DTG curves of PDCHI and the other two polymers. The single, irregularly shaped DTG peak of PDCHI indicates that the thermal degradation of this polymer is initiated by a reaction continuously yielding highly volatile products, probably originating from the substituents, as well as by random main chain scission. Both cyclohexane and cyclohexene have higher vapour pressures than other possible thermolysis products. The evolution of these vapours is to be expected, due to the structure of the monomer unit, *i.e.*, the tertiary hydrogen on the C1 atom of the cyclohexyl ring. This tertiary hydrogen is present in all three polymers, but it has different surroundings. Analysis of the volatiles revealed that depolymerization was the major degradation mechanism with almost 90 % monomer content.[35]

Relative changes in the mean molar mass of PDCHI and PDECHI during thermolysis are similar to those of the higher poly(di-*n*-alkyl itaconates). Increases in the mean molar mass are noticeable at lower degradation temperatures. At higher temperatures there more main chain scissions occur than crosslinks, so the overall effect is a mean molar mass decrease. Lateral macroradicals may form during bond scissions in the ester substituents. Such lateral macroradicals may combine, which implies that branching of the polymer is possible in the initial stages of degradation. At higher temperatures, carbonization is favoured.[35]
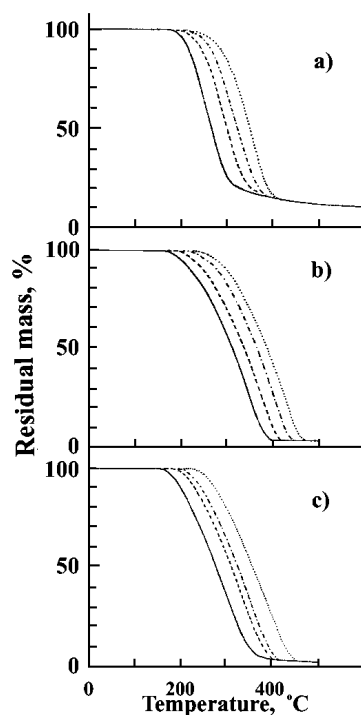
Fig. 20. Non-oxidative TG curves of poly(di-alkylcyclohexyl itaconates), a) PDCHI, b) PDMCHI and c) PDECHI. Heating rates 2.5 (——), 10 (-----), 20 (······) and 40 °C min⁻¹ (- · - ·). Nitrogen flow rate: 25 cm³ min⁻¹.[35]
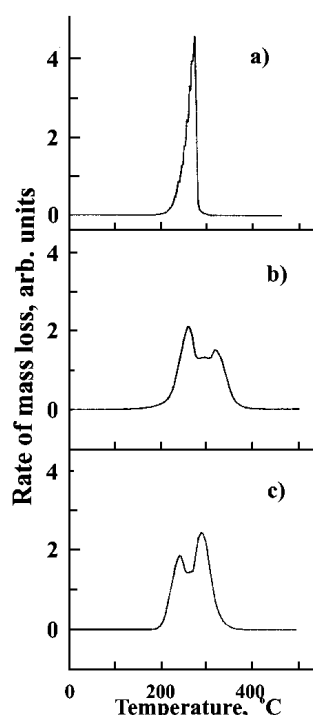
Fig. 21. Non-oxidative DTG curves of poly(di-alkylcyclohexyl itaconates), a) PDCHI, b) PDMCHI, and c) PDECHI. Heating rates 0.625 °C min⁻¹ (——). Nitrogen flow rate: 25 cm³ min⁻¹.[35]

7. POLY(DI-2-CHLOROETHYL ITACONATE)

The introduction of chlorine into the ester substituent of poly(di-itaconates) dramatically changes the thermal degradation mechanism.[36] The TG curves of poly(di-2-chloroethyl itaconate) (PD2CEI) become heating rate-dependent. The slope of the TG curve changes with heating rate, as does the amount of residue. The TG and DTG curves of PDCEI recorded at a very slow heating rate, at which the maximum amount of carbonaceous residue is obtained, are presented in Fig. 22. Even though the major thermolysis product is still monomer, the formation of a carbonaceous residue implies that crosslinking occurs. The DTG curve of PD2CEI is more complex than that of the single peak DTG curve of poly(2-chloroethyl methacrylate) (P2CMA).[37] It is interesting to note that the thermal degradation activation energy, E_a, of P2CMA is constant over mass loss, while the E_a of PDCEI continuously increases, which indicates that carbonization is occurring.[38] Isothermal degradation experiments were carried out in order to determine changes in mean molar mass or degree of crosslinking and to compare the two polymers, Fig. 23.
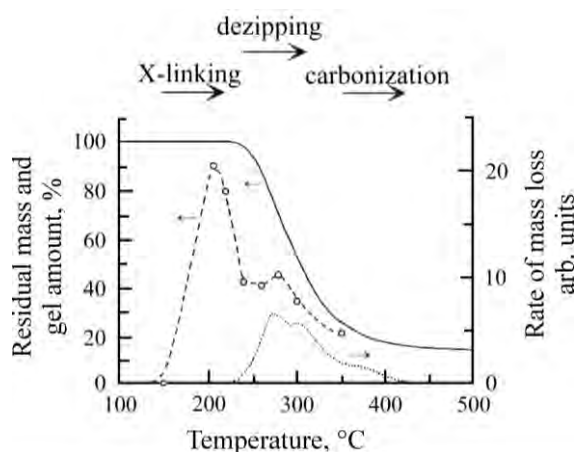
Fig. 22. Overall non-oxidative thermal degradation scheme of PD2CEI, TG (——) and DTG (-----) curves, heating rate 0.625 °C min^{-1}, amount of gel formed (% of initial polymer) (---○---), degradation time 45 min.[36]

During the thermal degradation of PD2CEI several processes occur simultaneously. Depolymerization competes with crosslinking up to 280 °C. At higher temperatures, main chain scission-initiated depolymerization is dominant. At temperatures greater than 280 °C, the residual crosslinked structures start to carbonize. The strong affinity to crosslinking can be related to the two ester substituents in the monomer unit of PD2CEI. Figure 22 explains the course of the degradation. The start of significant mass loss on the TG curve coincides with a decrease in the amount of formed gel. The first DTG peak coincides with the saddle in the gel content curve indicating extensive depolymerization. The second DTG peak or plateau corresponds to the second, smaller maximum of formed insoluble product, which can be related to simultaneous depolymerization and initial carbonization. The dominant process at higher temperatures is carbonization.
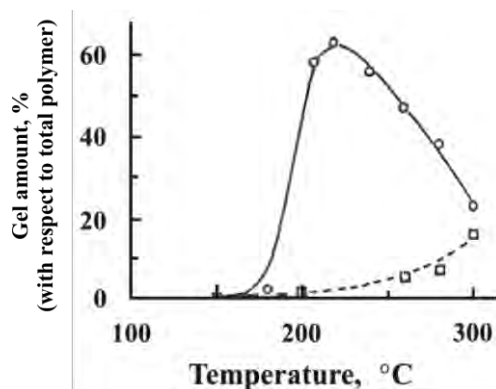

Fig. 23. Dependence of the amount of gel (% of initial polymer) on temperature, degradation time 30 min, PDCEI (○), P2CMA (□).[36]

8. CONCLUSIONS

The thermal degradation of poly(di-alkyl itaconates) was investigated in detail using numerous analytical techniques. Based on these investigations, a

general thermal degradation mechanism was proposed. It was established that the following reactions take place: depolymerization, ester decomposition, elimination, crosslinking, random main and/or side chain scission and carbonization. The susceptibility toward specific reactions depends on the structure of the ester substituent.

The basic and predominant process is depolymerization that may be initiated in several ways by end-chain or side chain scission. Ester decomposition becomes relevant when there are three or more β-hydrogens in the substituent. If crosslinking takes place at lower thermal degradation temperatures, carbonization is likely to occur at higher temperatures. A schematic presentation of the thermal degradation mechanism is presented below (Scheme 4).
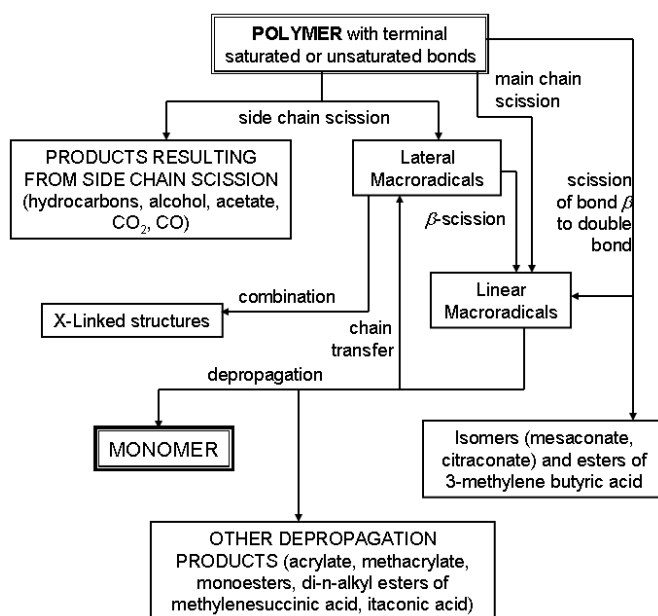
Scheme IV. Overall thermal degradation scheme of poly(di-alkyl itaconates).

И З В О Д

ТЕРМИЧКА РАЗГРАДЊА НЕКИХ ПОЛИМЕРНИХ ДИАЛКИЛ ЕСТАРА ИТАКОНСКЕ КИСЕЛИНЕ

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Једну групу полимера, који би могли да умање зависност од сирове нафте, чине полимери на бази итаконске киселине, чија биотехнолошка производња постаје исплатива. Итаконска киселина и њени деривати могу лако да се уграде у полимере и

могу да служе као замена за петрохемијски добијене акрилатне и метакрилатне мономере. Примена полимера на бази ди-естара итаконске киселине зависи у великој мери од њихове термичке стабилности. Термичка стабилност поли(ди-итаконата) зависи не само од опште структуре мономерне понављајуће јединице, већ и од структуре естарског супституента. Деполимеризација, иницирана кидањем или насумичним раскидањем везе у основном ланцу, је доминантан механизам термолизе у већини случајева. Деполимеризација поли(ди-итаконата) може да буде праћена де-естерификацијом, елиминацијом, умрежавањем, насумучним раскидањем везе у основном и/или бочном ланцу и карбонизацијом. Поређење механизма термичке разградње полимерних ди-естара итаконске киселине и одговарајућих полиметакрилата потврђује одрживост замене полиметакрилата поли(ди-итаконатима).

<div align="right">(Примљено 14. децембра 2013)</div>

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