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THE THERMAL DEGRADATION KINETICS OF POLY(CHLORETHYLMETHACRYLATES)

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The thermal degradation kinetics of poly(2–mono-, 2,2–di- and 2,2,2–trichlorethyl methacrylate) and of the non-chlorinated poly(ethyl methacrylate) were studied by TG in the absence and presence of oxygen. The overall thermal degradation energy, determined by the Flynn–Wall method, increases with increasing chlorine content of the polymer when the degradation is performed in the absence of oxygen, while the trend is reversed in the presence of oxygen. Competition between the two major non-oxidative thermolysis reactions, depolymerization and crosslinking, could be monitored by DTG. Generally, the thermal stability of the investigated polymers is reduced by oxygen.

Keywords: kinetics, poly(chlorethyl methacrylates)

Introduction

It is well known in the literature that poly(methacrylates) thermally decompose primarily by depolymerization [1]. In the case of poly(ethyl methacrylate) (PEMA) depolymerization is accompanied to a small extent by ester decomposition [2, 3]. The introduction of chlorine into the ester substituent affects the overall degradation mechanism. Some work on the thermal degradation of poly(chlorethyl methacrylates) was done by Chien *et al.* [4–6]. These studies were based on the analysis of samples pyrolysed at 600 °C. Thermal degradation studies of poly(2–mono, 2,2–di- and 2,2,2–trichlorethyl methacrylate) (PMCMA, PDCMA and PTCMA), designed to analyse the initial and intermediate stages of the process, have shown that depolymerization remains the dominant thermolysis reaction [7, 8].

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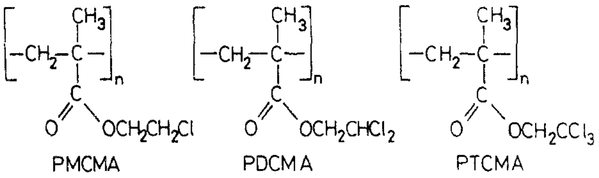

At degradation temperatures lower than 200 °C, in the absence of oxygen, the major process occurring in poly(chlorethyl methacrylates) is crosslinking. At higher temperatures the polymers predominantly depolymerize. Depolymerization is accompanied to a smaller extent by side chain scission and crosslinking [7].

In the presence of oxygen the degradation of PEMA is accelerated, while in the case of PTCMA crosslinking is prevented and depolymerization is retarded. In both cases oxidative main chain scission and depolymerization are the major degradation reactions, although the yield of monomer is somewhat lower than in the non-oxidative case and the number and abundance of other volatile products greater. The formation of the corresponding ester of 2–methoxy-oxirane carbonic acid is one of the preferred side reactions [8].

The influence of the presence of chlorine in the ester substituents on the thermal stability and thermal degradation kinetics of poly(chlorethyl methacrylates) will be discussed in this paper.

Experimental

2–Mono, 2,2–di- and 2,2,2–trichlorethyl methacrylate were prepared by the standard esterification of methacrylic acid (Aldrich, p.a.) with the corresponding alcohol (all Aldrich, p.a.) in benzene. Ethyl methacrylate (Merck, p.a.) was freed from inhibitor and distilled before further use.

Table 1 Chlorine contents and molar masses of the initial polymers

Polymer	Cl found / %	Cl calculated / %	M_w	M_w/M_n
PMCMA	23.7	23.9	$1.1\cdot10^6$	3.8
PDCMA	38.0	38.8	$3.4\cdot10^6$	3.3
PTCMA	48.0	49.0	$1.7\cdot10^5$	4.4
PEMA	–	–	$1.3\cdot10^6$	3.2

The polymers were obtained by polymerizing the monomers in bulk at 35 °C with 0.5 mol% α,α'–azobisisobutyronitrile as initiator in ampules sealed under high vacuum. The polymerisations were taken to low yields of not more than 15%. The composition of the obtained polymers was confirmed by determinations of the chlorine content (Table 1). The molar masses of the polymers were determined by gel permeation chromatography (Knauer/Trilab) using poly(methyl methacrylate) samples (Röhm GmbH, Germany) as standards (Table 1).

A Perkin Elmer TGS–2 instrument was used for the thermogravimetric measurements. Non-isothermal experiments were performed in the temperature range 30 °C to 500 °C at heating rates of 2.5, 10, 20 and 40 $\text{deg}\cdot\text{min}^{-1}$. The DTG runs were done at 0.625 $\text{deg}\cdot\text{min}^{-1}$.The average sample size was 5 mg and the gas (nitrogen or air) flow rate 20 cm^3/min. The thermogravimetric data were analysed by the Flynn–Wall method [9]. This is a fast and simple method which enables the determination of thermal degradation activation energies on the basis of three or more thermogravimetric runs performed at different heating rates. The activation energy was derived from the slope of the dependence of the heating rate, $\log\beta$, upon the reciprocal absolute temperature, $1/T$, at a defined mass loss. The presented activation energies of thermal degradation, E_a, are mean values of, on average, nine values.

The thermal degradation set-up and applied product analysis techniques are described elsewhere [7, 8].

Results and discussion

Degradation in inert atmosphere

The non-isothermal thermogravimetric (TG) curves of PMCMA, PDCMA, PTCMA and PEMA, obtained at various heating rates, are presented in Fig. 1. The TG curves of PMCMA and PTCMA are smooth with uniform slopes. The shape of the PDCMA TG curve indicates a two phase decomposition process. In the case of PEMA, three changes in the slope of the TG curves can be registered. The slopes of the TG curves are independent of the heating rate.

The temperatures of 5, 50 and 90% mass losses at a heating rate of 2.5 $\text{deg}\cdot\text{min}^{-1}$ for all four polymers are given in Table 2. At 500 °C carbonized residues of 1 to 2% of the mass of the initial polymer were registered in all cases except PDCMA where a 6% residue was recorded.

In conjunction with the shapes of the TG curves, uniform, conversion independent values of the E_a were found in the cases of PMCMA and

PTCMA, 83±2 kJ·mol^{-1} and 100±5 kJ·mol^{-1}, respectively. The E_a of the first phase of the thermal degradation of PDCMA was 92±3 kJ·mol^{-1} and that of the second 214±8 kJ·mol^{-1}. The E_a of PEMA, 74±7 kJ·mol^{-1}, was uniform up to mass losses of about 80% after which the E_a increased.

Table 2 Characteristic mass loss temperatures of the investigated polymers, heating rate 2.5 deg·min^{-1}, gas flow rate 20 cm^3·min^{-1}

Polymer	$T_{5\%}$		$T_{50\%}$		$T_{90\%}$	
	Inert	Air	Inert	Air	Inert	Air
PMCMA	243	236	288	261	309	286
PDCMA	225	211	283	240	426	320
PTCMA	238	231	266	245	288	257
PEMA	231	200	282	235	362	302

Comparison of the E_a values obtained for the polymer mass loss region up to 70% indicates that the E_a increases linearly with increasing number of chlorine atoms in the end group of the ester substituent (Fig. 2). This change could be caused by a chlorine induced electron withdrawing effect in the polymer side chains.

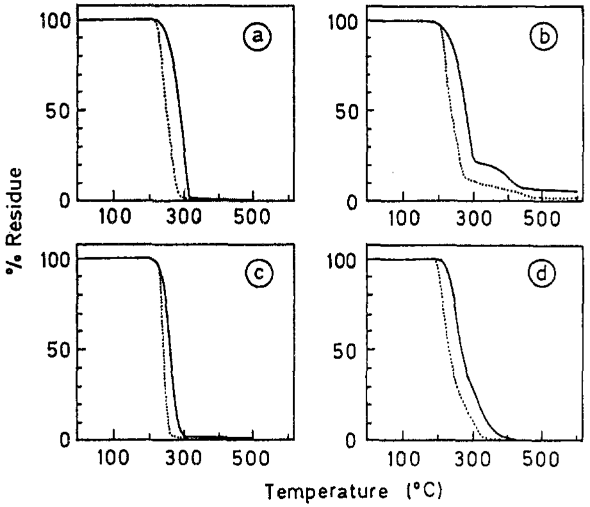

Fig. 1 Non-isothermal thermogravimetric curves of a) PMCMA, b) PDCMA, c) PTCMA and d) PEMA in the absence (———) and presence (– – –) of oxygen, heating rate 2.5 deg·min^{-1}, nitrogen flow rate 20 cm^3/min

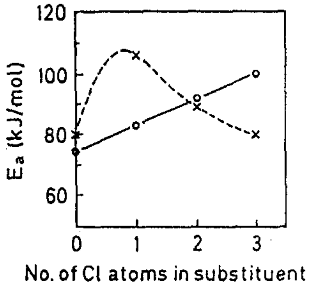

Fig. 2 Dependence of the E_a on the number of chlorine atoms in the ester substituent of poly(chlorethyl methacrylates) in the absence (——) and presence of oxygen (– – –)

Changes in the degradation kinetics can also be seen by analysing the differential thermogravimetric (DTG) curves (Fig. 3, Table 3). The DTG curve of PMCMA consists of a single asymmetric peak the upward slope of which changes at about 246 °C. In the case of PDCMA there are two DTG peaks. The larger one is asymmetric and has a change in upward slope at about 245 °C, while the smaller one is much broader than the larger one. The DTG curve of PTCMA consists of a single symmetric peak. In the case of the DTG curve of PEMA, after the first larger symmetric peak, a plateau is registered between 292 °C and 318 °C, which decreases and leads into a second smaller peak. It is interesting to note that the temperature at which changes in the upward slopes of PMCMA and PDCMA were registered,

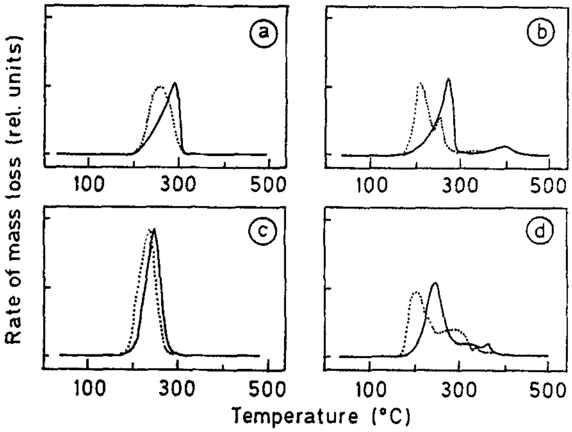

Fig. 3 Differential thermogravimetric curves of a) PMCMA, b) PDCMA, c) PTCMA and d) PEMA in the absence (——) and presence (– – –) of oxygen, heating rate 0.625 deg·min^{-1}, gas flowrate 20 cm^3·min

245 °C, coincides with the values of the DTG maxima of PTCMA and PEMA.

The major thermolysis processes of poly(chlorethyl methacrylates) have been found to be depolymerization and crosslinking. Depending on the number of chlorine atoms in the ester substituent, the extent of these two reactions differs as does the tendency towards minor reactions in the side groups.

The thermolysis reactions in the side chains in the case of PMCMA are dehydrochlorination and/or dechlorination followed by the formation of acetaldehyde and carbon monoxide and/or ethylene and carbon dioxide, in the case of PDCMA dehydrochlorination and/or dechlorination followed by the formation of chloracetaldehyde and carbon monoxide and in the case of PTCMA cleavage of the trichlormethyl group and the formation of methyl methacrylate.

Table 3 DTG maxima of the investigated polymers in the absence and presence of oxygen, heating rate 0.625 deg·min^{-1}, gas flow rate 20 cm^3·min^{-1}

Polymer	T_{max1} / °C		T_{max2} / °C	
	Inert	Air	Inert	Air
PMCMA	286	241	–	–
PDCMA	270	208	393	243
PTCMA	246	238	–	–
PEMA	244	196	367	283

At lower degradation temperatures crosslinking dominates over main-chain scission and depolymerization as evidenced by the increase in molar mass and subsequent insolubilization of the polymers. The susceptibility to crosslinking of the investigated polymers differs as shown by the residual gel contents (Fig. 4a).

With increasing degradation temperature and heating time, chain scission becomes more effective as manifested by a decrease in the relative crosslink densities of PMCMA and PDCMA (Figs 4b and 4c).

The competition between these reactions is also reflected in the DTG curves of PMCMA and PDCMA. Changes, i.e. increases in the upward slopes of the curves of both of these polymers lie at approximately the same temperature, 245 °C, i.e. the temperature at which PTCMA, which crosslinks only to a very small extent, and PEMA, which does not crosslink at all, have their DTG maxima. The rate of mass loss of PMCMA and PDCMA at temperatures lower than 245 °C is reduced due to the opposing effects of simultaneous crosslinking and chain scission. When the threshold temperature is passed, polymer size reducing processes prevail and accelerate the mass loss. These crosslinking effects in the cases of PMCMA and PDCMA are responsible for the shift of the DTG maxima to higher temperatures.

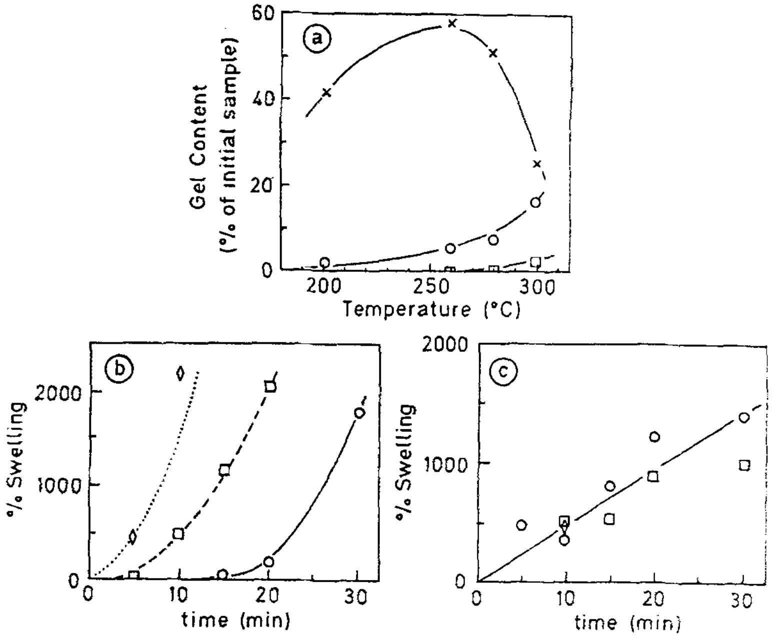

Fig. 4 Thermal degradation of poly(chlorethyl methacrylates): a) amounts of gel (% of initial sample) formed during the degradation of (o) PMCMA, (x) PDCMA and PTCMA (□), heating time 30 min, and the swelling of PMCMA (b) and PDCMA (c) gels formed as a consequence of heating at (o) 200 °C, (□) 260 °C and (◇) 280 °C in the absence of oxygen

The affinity toward depolymerization is opposite to that of crosslinking. After 30 minutes of heating the polymer samples at 260 °C, the amounts of monomer in the volatile mixtures are 83, 77 and 94% for PMCMA, PDCMA and PTCMA, respectively.

Of the investigated polymers only PDCMA has a distinct second decomposition stage. At temperatures higher than 280 °C the accumulated highly crosslinked network structure starts to decompose yielding methane and aromatic structures leaving a carbonized residue that is stable at 600 °C.

Degradation in oxidative atmosphere

When the investigated polymers are heated in air (Fig. 1), initial mass losses are registered at lower temperatures than those degraded in inert atmosphere (see Table 1). At 500 °C not more than a 2% carbon residue is registered in all the polymers.

The mean values of the E_a of poly(chlorethyl methacrylates) decrease with increasing number of chlorines in the ester substituent. The calculated values of E_a are 106 ±19, 89 ±16 and 80 ±7 $\text{kJ}\cdot\text{mol}^{-1}$ for PMCMA, PDCMA and PTCMA, respectively. The E_a of PEMA, 80 ±6 $\text{kJ}\cdot\text{mol}^{-1}$, is uniform up to mass losses of 80% and does not relevantly vary from the non-oxidative value.

Some of the DTG curves of poly(chlorethyl methacrylates) heated in air differ to those decomposed in inert atmosphere (Fig. 3). The shapes of the DTG curves of PEMA and PTCMA do not change significantly. The DTG curve of PMCMA is now symmetric, while the PDCMA one consists of two adjoining symmetric peaks of different intensity. All the DTG maxima are shifted toward lower temperatures.

Conclusions

The investigated polymers were found to be less thermally stable in air than inert atmosphere. More information on the oxidative thermolysis of PMCMA and PDCMA is required before detailed conclusions about the oxidative thermal stability of poly(chlorethyl methacrylates) can be made.

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Zusammenfassung — Mittels TG wurde in Gegenwart und in Abwesenheit von Sauerstoff die Kinetik des thermischen Abbaues von Poly(2-mono, 2,2-di- und 2,2,2-trichlorethylmethacrylat) und des nichtchlorierten Poly(ethylmethacrylat) untersucht. Die mit der Flynn-Wall Methode bestimmte Gesamtenergie des thermischen Abbaues steigt mit wachsendem Chlorgehalt des Polymers, wenn der Abbau ohne Sauerstoff erfolgt. In Gegenwart von Sauerstoff wird dieser Trend genau umgekehrt. Mittels DTG konnten die zwei wichtigsten nichtoxidativen Thermolysereaktionen, Depolymerisierung und Vernetzung, als kompetitive Reaktionen nachgewiesen werden. Ganz allgemein wird die thermische Stabilität der untersuchten Polymere durch Sauerstoff herabgesetzt.