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The thermal degradation of poly(*iso*-butyl methacrylate) and poly(*sec*-butyl methacrylate)

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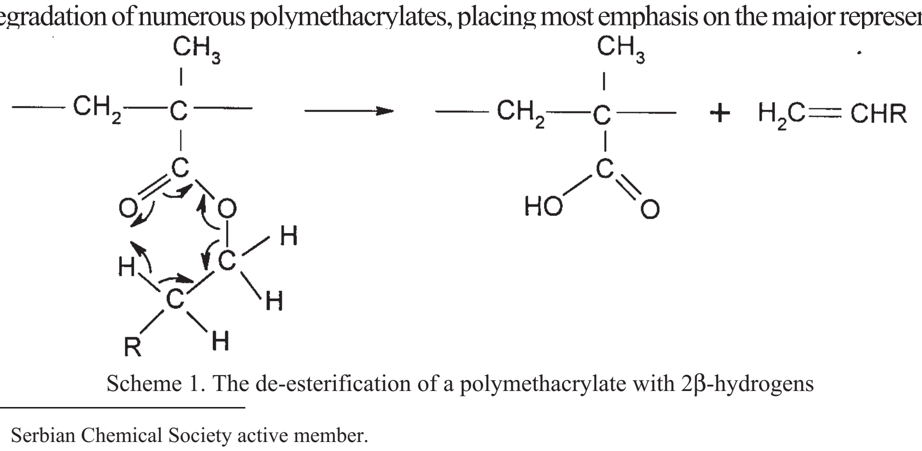
The non-oxidative thermal degradation of poly(*iso*-butyl methacrylate) and poly(*sec*-butyl methacrylate) was investigated by studying changes in the polymer residue. Due to the different number of β-hydrogens in their ester substituents, these two polymeric isomers behave differently when subjected to elevated temperatures. Poly(*iso*-butyl methacrylate) degrades quantitatively by depolymerisation with zip lengths of the same order of magnitude as those of poly(methyl methacrylate). Poly(*sec*-butyl methacrylate) degrades by a combined degradation mechanism of depolymerisation and de-esterification. De-esterification becomes a significant thermolysis route at temperatures higher than 240 ºC.

Keywords: poly(butyl methacrylate), isomers, thermal degradation, mechanism, depolymerisation, de-esterification.

INTRODUCTION

It is generally considered that most polymethacrylates thermally degrade by depolymerisation. Grassie and his co-workers initiated and carried out investigations of thermal degradation of numerous polymethacrylates, placing most emphasis on the major represen-



Scheme 1. The de-esterification of a polymethacrylate with 2β-hydrogens

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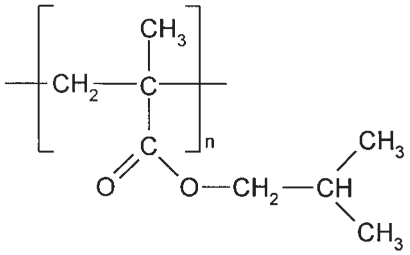
tative of this class of compounds, poly(methyl methacrylate) (PMMA).[1–4] Although PMMA degrades practically quantitatively to its monomer, the thermolysis mechanism of other polymethacrylates is not that simple and is determined predominantly by the structure of the ester substituent. If there are β-hydrogen atoms present in the substituent, de-esterification may and does occur (Scheme 1).

The influence of β-hydrogens on the thermolysis mechanism of polymethacrylates is shown in Table I.[3] De-esterification competes with depolymerisation as a relevant degradation path when the monomer unit has five or more β-hydrogens. Consequently, isomeric structures such as poly(*iso*-, *n*-, *sec*- and *tert*-butyl methacrylate) (PiBMA, PnBMA, PsBMA and PtBMA) have different thermolysis mechanisms. Grassie studied the thermal degradation of PnBMA nad PtBMA and found that the former predominantly degraded by depolymerisation[2] and the latter by de-esterification.[5]

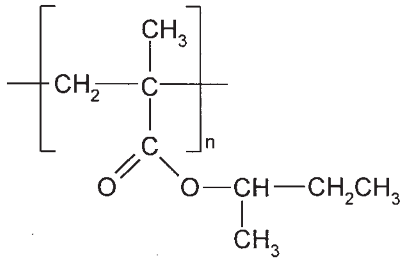
TABLE I. The influence of β-hydrogens on the thermal degradation mechanism of polymethacrylates[3]

Depolymerisation		Mostly depolymerisation		De-esterification	
Substituent	No. of β-Hs	Substituent	No. of β-Hs	Substituent	No. of β-Hs
Methyl	0	Ethyl	3	*iso*-Propyl	6
Neopentyl	0	*n*-Propyl	2	*sec*-Butyl	5
iso-Butyl	1	*n*-Butyl	2	*tert*-Butyl	9
Ethoxyethyl	2	*n*-Hexyl	2		
		n-Heptyl	2		
		n-Octyl	2		

The goal of this study was to investigate the thermal degradation of PiBMA (Structure I) and PsBMA (Structure II) and determine their basic thermolysis mechanisms by studying changes in the polymer residue.



Stucture I



Stucture II

EXPERIMENTAL

The monomers, *iso*-butyl methacrylate and *sec*-butyl methacrylate, were synthesised by the standard acid catalysed esterification of methacrylic acid (Aldrich, p.a.) with *iso*-butanol (Kemika, p.a.) and *sec*-butanol (Kemika, p.a), respectively. After the normal work-up procedure, the monomers were vacuum distilled immediately prior to polymerisation. The polymerisations were performed in bulk at 50 ºC in glass ampoules sealed under high vacuum using 0.5 mol % α,α'-azobisisobutyronitrile (AIBN) as the initiator. The polymers were isolated by precipitation with methanol (Zorka Pharma, p.a.) containing about 5 % water and freed of residual monomer by repeated precipitation from acetone (Zorka Pharma, p.a.) solutions using methanol containing 5 % water. The polymers were dried to constant mass at room temperature.

The values of the limiting viscosity numbers (LVN) of the samples were determined in acetone at 25 ºC using an Ubbelohde viscometer; $LVN_{PiBMA} = 0.123\ m^3/kg$ and $LVN_{PsBMA} = 0.0686\ m^3/kg$. The mean number-average molar mass, $\overline{M}_n$ of PiBMA was calculated from the obtained LVN value using the Kuhn-Mark-Houwink-Sakurada equation and literature values for the coefficients K and a[6]; $\overline{M}_n = 4.33 \times 10^5$ g/mol.

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 ±1ºC. Experiments were performed in the range 180 – 200 ºC for PiBMA and 200 – 260 ºC for PsBMA under a nitrogen flow of 50 cm^3/min for 5 to 30 min. The sample masses were about 120 mg.

After determining the mass loss, the PiBMA residues were analysed by measuring the LVN. The content of free acid groups in degraded PsBMA samples was determined by dissolving or swelling the residue in methanol, adding a known amount of methanolic 0.1 mol/dm^3 NaOH solution and back titrating the excess alkali with 0.1 mol/dm^3 aqueous HCl using phenolphthalein as indicator.

RESULTS AND DISCUSSION

Thermal degradation of PiBMA

The isothermal mass loss of PiBMA as a function of degradation time at various thermolysis temperatures is shown in Fig. 1. Significant mass loss can be noticed at longer degradation times and at 200 ºC. Based on the fact that PiBMA has one β-hydrogen in its ester substituent, it may be assumed that depolymerisation is the main thermal degradation mechanism. This assumption was confirmed by thermal volatilisation analysis (TVA), which indicated almost quantitative degradation to monomer.[7] Therefore, it is interesting to follow changes in the molar mass of the residue during thermal degradation, Fig. 2. The molar mass of PiBMA decreases considerably during degradation.

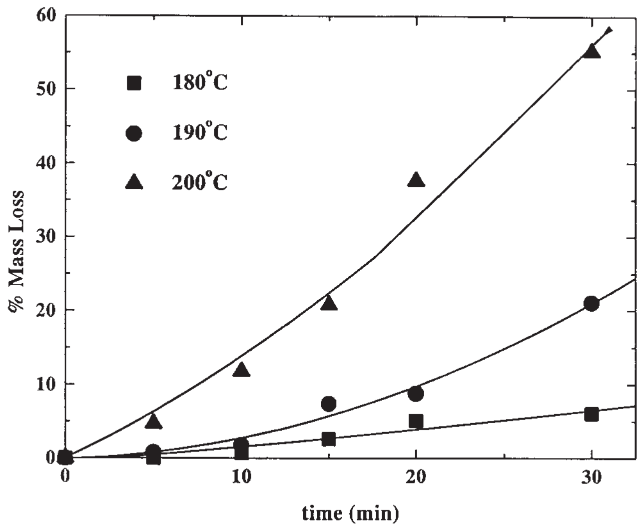


Fig. 1. The dependence of PiBMA mass loss on time at various degradation temperatures.

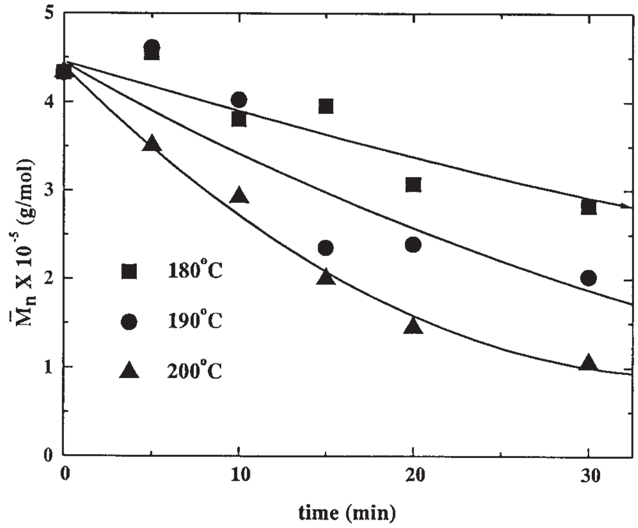


Fig. 2. The change in $\overline{M}_n$ of PiBMA degraded at various temperatures.

The number of main chain scissions per monomer unit can be determined on the basis of changes in the mass and molar mass of the degraded sample.[8] The number of bond scissions per monomer unit, s/P_0, may be calculated from the equation:

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

where s is the number of scissions, x the fraction of evaporated thermal degradation volatiles, and P_0 and P_t the degrees of polymerisation of the initial and degraded polymer, respectively. The results of this calculation are shown in Fig. 3 where s/P_0 is plotted against time at various temperatures. It may be noticed that the values of

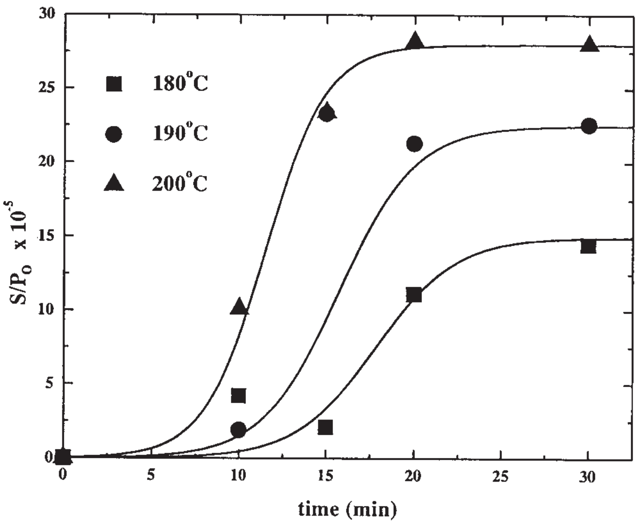


Fig. 3. Dependence of the number of bonds broken per monomer unit of PiBMA, s/P_0, on time at various degradation temperatures.

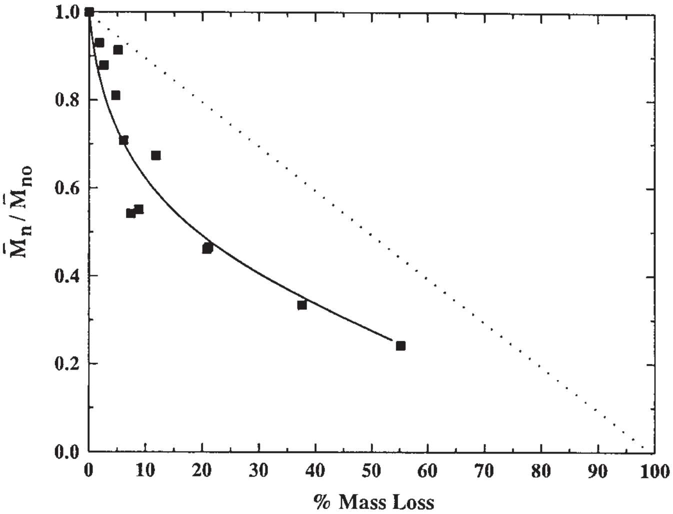


Fig. 4. The relative change of PiBMA molar mass, $\overline{M}_n/\overline{M}_{n0}$, as a function of mass loss after thermal treatment.

s/P_0 tend toward constant values at longer degradation times. As expected, higher values of s/P_0 are observed at higher degradation temperatures.

The relative change in the molar mass of the polymer residues, $\overline{M}_n/\overline{M}_{n0}$, as a function of mass loss is shown in Fig. 4. The shape of the $\overline{M}_n/\overline{M}_{n0}$ *vs*. conversion curve indicates the occurrence of random main chain scission, which initiates depolymerisation, and/or that the zip length of depropagation, Z, is smaller than the degree of polymerisation of the polymer.[8]

An attempt was made to determine the zip length of depropagation by the equation proposed by Kashiwagi *et al*.:[9]

$$\frac{W}{W_0} = \frac{P_t^2}{P_0^2}\left(\frac{Z+P_0}{Z+P_t}\right)^2 \tag{2}$$

where W/W_0 is the ratio of the mass of the residue and the mass of the initial polymer. The results of the calculation are shown in Fig. 5. The value of Z increases with degradation temperature. Also, as expected from the shape of the dependence $\overline{M}_n/\overline{M}_{n0}$ *vs*. mass loss, the values of Z are lower than the initial degree of polymerisation of PiBMA, P_0 = 3050. Similar calculations for PMMA degraded in the temperature range 260–300 ºC yielded Z values between 1000 and 2000.[9] The values for PiBMA are lower most probably because they were derived from data obtained at lower thermolysis temperatures. If one extrapolates the obtained depencence of Z *vs*. degradation temperature to the temperatures 260 and 300 ºC, one obtains Z values of 1455 and 2080, respectively, which compare very well with the values determined for PMMA and indicate the similar depropagation behaviour of PMMA and PiBMA.

However, detailed results obtained for the thermolysis of the structurally similar isomeric butyl diesters of poly(itaconic acid) showed that although depolymerisation

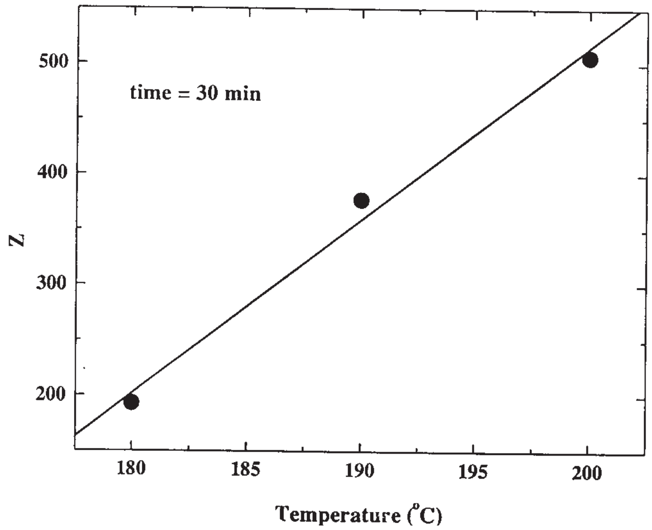


Fig. 5. The depencence of the depolymerisation zip length Z on temperature after a degradation time of 30 min.

was the main degradation mechanism of poly(di-isobutyl itaconate) (PDiBI) more alkene was evolved than was the case of poly(di-*n*-butyl itaconate) (PDnBI).[10] This is contrary to the assumption that the amount of ester decomposition is dependent on the number of β-hydrogen atoms. This fact was explained by the special lability of the lone tertiary hydrogen atom present in the ester substituents of PDiBI. This mechanism is also likely to accur in the thermal degradation of PiBMA. Furher results would be necessary to confirm this assumption.

Thermal degradation of PsBMA

The isothermal mass loss of PsBMA as a function of degradation time at various thermolysis temperatures is shown in Fig. 6. Significant mass loss can be noticed at 220 °C.

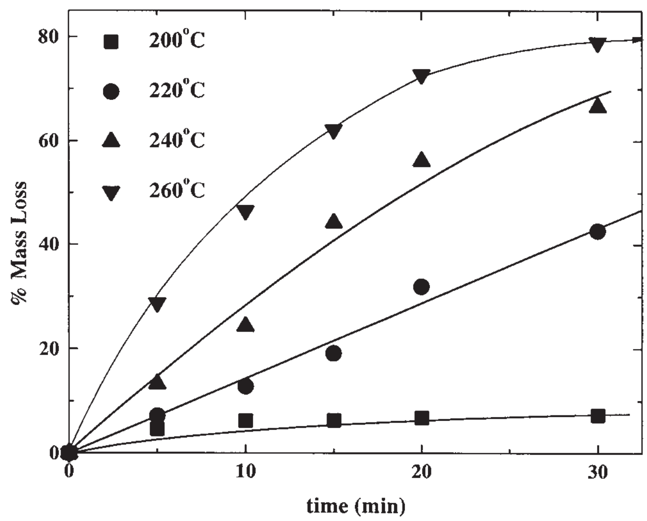


Fig. 6. The dependence of PsBMA mass loss on time at various degradation temperatures.

Compared to PiBMA, PsBMA seems to be more thermally stable (the mass loss of PiBMA after 30 min at 200 ºC is 55.2 % and for PsBMA 7.4 %). As PsBMA has five β-hydrogens in the ester substituent, it may be assumed that de-esterification significantly competes with depolymerisation as the main thermal degradation mechanism.

Attempts to determine the LVN of degraded PsBMA were not successful as η_{sp}/c increased with decreasing polymer concentration. Such behaviour indicates that the structure of the polymer residue changes during thermal degradation implying that depropagation is not the only degradation mechanism and that the residue has ionometric properties in dilute solution. The ionomeric properties can only result from the existence of free acid or anhydride groups in the polymer residue.

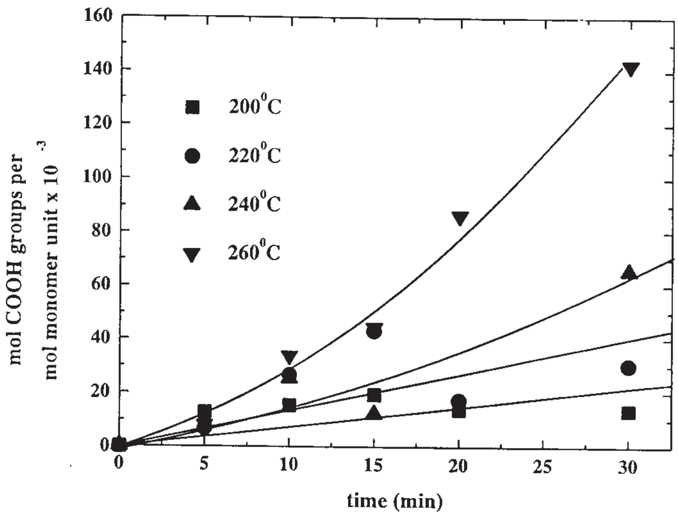


Fig. 7. The dependence of the number of COOH groups evolved per monomer unit of PsBMA as a function of time at various thermolysis temperatures.

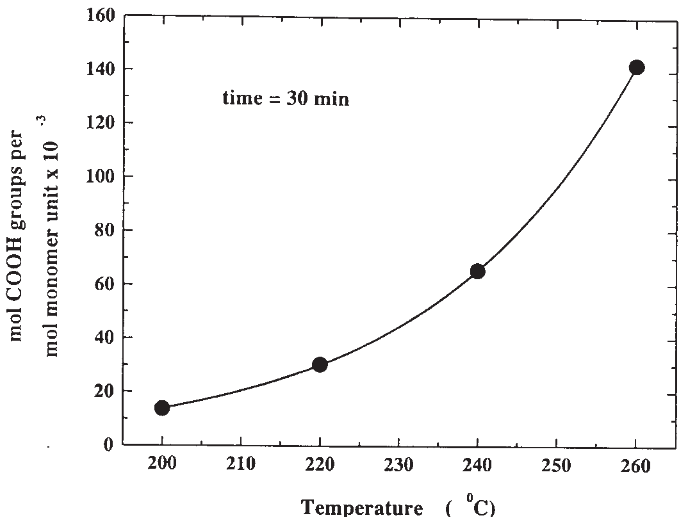


Fig. 8. The depencence of the number of COOH groups evolved per monomer unit of PsBMA as a function of temperature, degradation time 30 min.

The acid gropus formed in the PsBMA residue were determined quantitatively by acid-base titrations of the residues. The determined amounts of acid groups, expressed as mol COOH per mol monomer unit, are shown as a function of time and temperature of degradation in Figs. 7 and 8, respectively. The number of evolved COOH groups increases exponentially with degradation temperature indicating that de-esterification is a relevant degradation route at temperatures higher than 240 ºC. These data agree well with the TVA data of McNeill on the evolution of 1- and 2-butene during thermolysis.[7] Similar behaviour was found for the thermal degradation of the structurally similar poly(di-*sec*-butyl itaconate).[10]

CONCLUSIONS

On the basis of our own findings and the TVA work of McNeill,[7] it may be concluded that the assumptions made by Grassie and coworkers[1–4] concerning the mechanism of thermal degradation of polymethacrylates were generally correct, although the importance of the lone tertiary hydrogen atom in the ester substituent structures still needs to be established. Poly(*iso*-butyl methacrylate) degrades quantitatively by depolymerisation with zip lengths of the same order of magnitude as those of PMMA. Poly(*sec*-butyl methacrylate) degrades by a combined degradation mechanism of depolymerisation and de-esterification. De-esterification becomes a significant thermolysis route at temperatures higher than 240 ºC.

И З В О Д

ТЕРМИЧКА ДЕГРАДАЦИЈА ПОЛИ(*iso*-БУТИЛ МЕТАКРИЛАТА) И ПОЛИ(*sec*-БУТИЛ МЕТАКРИЛАТА)

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Неоксидативна термичка деградација поли(*iso*-бутил метакрилата) и поли(*sec*-бутил метакрилата) испитана је праћењем промена у полимерном остатку. Због различитог броја β-водоника у естарском супституенту, ова два полимерна изомера се различито понашају приликом излагања повишеним температурама. Поли(*iso*-бутил метакрилат) деградира квантитативно деполимеризацијом до свог мономера са кинетичким дужинама депропагације истог реда величине као код деградације поли(метил метакрилата). Поли(*sec*-бутил метакрилат) деградира комбинованим механизмом деградације: деполимеризацијом и деестерификацијом. Деестирификација постаје значајна реакција термолизе на температурама вишим од 240 ºC.

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