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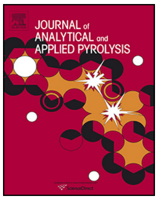

# Thermal degradation of poly(n-butyl methacrylate), poly(n-butyl acrylate) and poly(t-butyl acrylate)

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ABSTRACT

Direct pyrolysis mass spectrometry findings revealed that thermal decompositions of poly(n-butyl methacrylate), PnBMA, poly(n-butyl acrylate), PnBA, and poly(t-butyl acrylate), PtBA, follow different decomposition pathways. Among these polymers thermal degradation via depolymerization is only major decomposition routes for PnBMA. Thermal degradation of PnBA proceeds through simultaneous and subsequent processes, involving γ-hydrogen transfer to carbonyl group from the main chain to carbonyl groups yielding mainly six-membered cyclic products and butanol. On the other hand, decomposition of PtBA starts by elimination of $C_4H_8$ by γ-hydrogen transfer reactions from the t-butyl groups to the carbonyl groups producing poly(acrylic acid) chains by elimination of isobutene. Subsequent losses of $H_2O$, $CO_2$ and CO yield unsaturated linkages and crosslinked structures that decompose at elevated temperatures.

## 1. Introduction

Polyacrylates, because of their wide applications in paint, paper, adhesive, textile, and leather industries have been studied extensively. The knowledge of thermal and photo-oxidative degradation behavior of acrylic polymers enables their effective use and understanding the life cycle of the products or disposing of the product after end use and recycling of polymers. The pyrolytic thermal degradation of polyacrylates and their copolymers in nitrogen, oxygen and vacuum has been extensively studied by many research groups [1–24].

Manring proposed that the random scission degradation of PMMA is initiated by homolytic scission of a methoxycarbonyl side group followed by β scission rather than by main chain scission in the temperature range 350–400 °C [2]. Holland and Hay concluded that the degradation of PMMA was initiated by a mixture of chain-end and random scission, followed by depropagation and first-order termination at low temperatures below 360 °C, whereas initiation was a mixture of chain end and chain scission processes, followed by depropagation to the end of the polymer chain at temperatures above 385 °C [3].

Grassie studied thermal degradation of some poly(alkyl acrylate)s and poly(alkyl methacrylate)s by analyzing separated gaseous and liquid products by mass and IR spectroscopy [5–7]. Haken and Tan determined via a Curie point pyrolyzer in conjunction with a gas chromatography–mass spectrometry that the predominant pyrolysis products of poly(butyl acrylate) and its isomer are carbon dioxide, monomer and dimer and isobutylene [8]. Lehrle and Place proposed that random scissions do not play a significant part in the mechanism for the thermal degradation of PMA and the depropagation, accompanied by intramolecular transfer, is the predominant degradation pathway [9–11].

Mahalik et al. studied the thermal degradation of PMA and PBA homopolymers with TGA in order to investigate the effect of the alkyl group chain length [12]. The thermal degradation of PBA and PMA was investigated by pyrolysis and in solution and it was found that the degradability of the polymer decreases with an increase in the alkyl group chain length of poly(*n*-alkyl acrylate).

In a more recent study, thermal degradation of some alkyl metacrylates was investigated by Czech and Pełech in temperatures between 300 and 800 °C by pyrolysis gas chromatography [14]. They determined that during the thermal degradation, poly(alky methacrylates) produce the monomer as the main product in all tested pyrolysis conditions and an increase in pyrolysis temperature leads to higher yields of products derived from the main and side chains decomposition such as carbon dioxide, carbon monoxide, methane, ethane, or low molecular weight alcohols.

It has also been determined by Bertini and coworkers that unlike poly(methyl methacrylate) which gives quantitative yields of monomer, the poly-n-alkyl methacrylates with longer alkyl chain produce also significant amounts of olefin and methacrylic acid [15]. Recently, Soeriyadi et al. studied thermal degradation of poly(methyl methacrylate) (PMMA), poly(n-butyl methacrylate)

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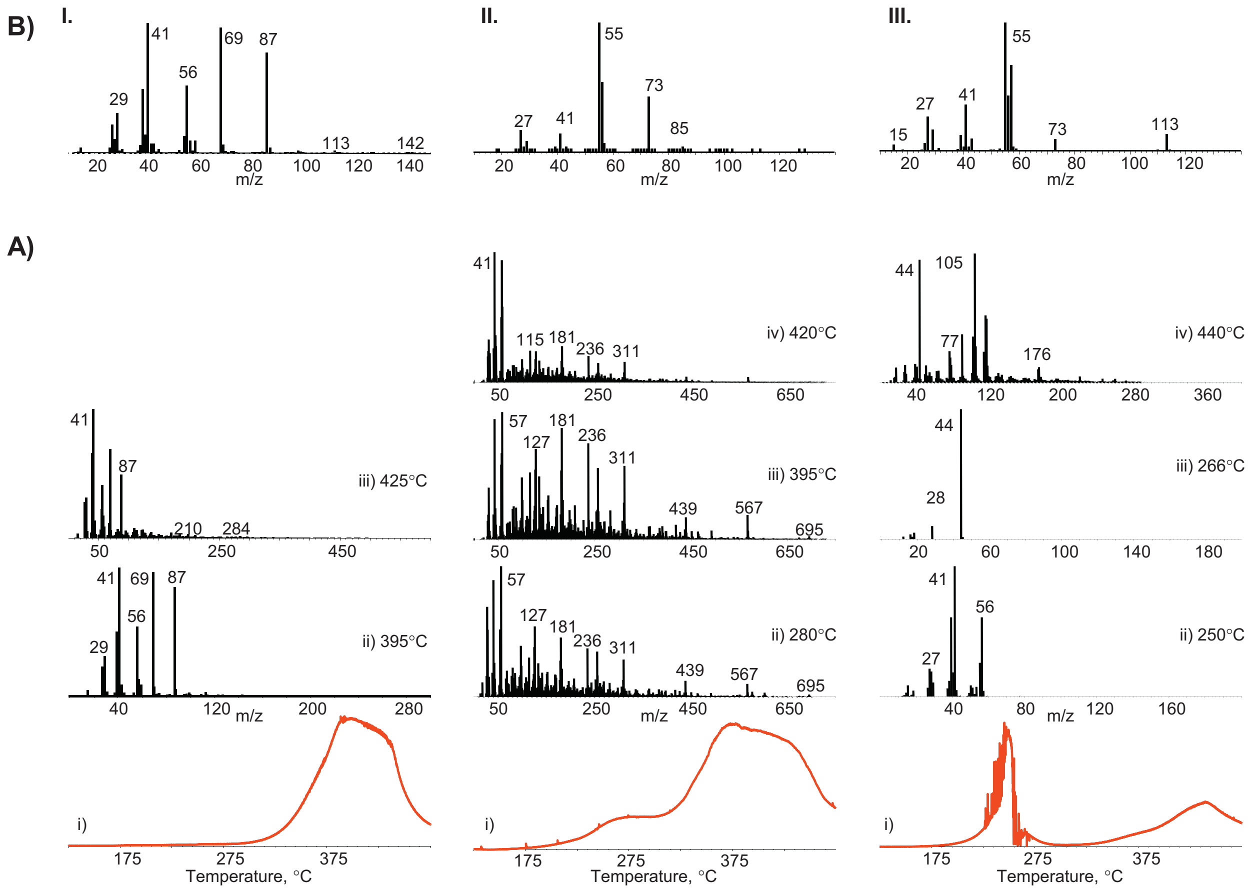

**Fig. 1.** (A) The TIC curves and the mass spectra at peak maxima and at shoulders present in the TIC curve recorded during the pyrolysis of (I) PnBMA, (II) PnBA, and (III) PtBA, and (B). The mass spectra of monomers; (I) nBMA, (II) nBA and (III) tBA.

(PBMA), poly(n-butyl acrylate) (PBA), and poly(lauryl methacrylate) (PLMA) and suggested that the general degradation mechanism involves the loss of the ester side groups to form methacrylic acid followed by cross-linking [16]. The effect of the variable end groups was found to be minimal whereas significant differences in the degradation between PBA and PBMA were observed.

In almost all research work on thermal degradation of poly(alkyl acrylate)s and poly(alkyl methacrylate)s classic thermal analysis techniques such as TGA, pyrolysis GC, pyrolysis FTIR or pyrolysis GC–MS techniques were applied. All these techniques only enable the detection of stable decomposition products and suffer in identifying the primary thermal degradation products. Among the several techniques used to investigate thermal degradation products, only in the case of direct pyrolysis mass spectrometry (DP-MS) technique, secondary and condensation reactions are almost totally avoided. Hence, detection of high mass pyrolyzates and unstable thermal degradation products are possible [25,26]. Thus, a better understanding of the thermal characteristics, polymerization, crosslinking and char formation processes can be achieved.

The objective of this study is to investigate systematically the thermal degradation process of poly(n-butyl acrylate) PnBA, poly(t-butyl acrylate), PtBA, and poly(n-butyl methacrylate), PnBMA selected as model compounds in order to investigate the effects of structure of side chain and methyl substitution on thermal degradation mechanism via direct pyrolysis mass spectrometry.

## 2. Experimental

Poly(n-butyl acrylate) was prepared by polymerization of n-butyl acrylate (Aldrich), purified by passing through a basic poly(n-butyl methacrylate), via free-radical polymerization using azo-bis-(isobutyronitril) (AIBN) and n-dodacene mercaptan as the initiator and chain transfer agents, respectively. Poly(n-butyl methacrylate) (Mn = 1500, Mw = 1700 PI = 1.2) and poly(t-butyl acrylate) (Mn = 13,000, Mw = 14,500 PI = 1.1) were received from Polymer Source and used as received.

Direct pyrolysis mass spectrometry (DPMS) analyses were performed on a 5973 HP quadrupole mass spectrometry system coupled to a JHP SIS direct insertion probe pyrolysis system. 70 eV EI mass spectra, at a rate of 2 scan $s^{-1}$, were recorded. 0.01 mg samples in the flared glass sample vials were heated to 450 °C at a rate of 10 °C $min^{-1}$. The pyrolysis mass spectrometry analyses were repeated at least two times to ensure reproducibility.

## 3. Results and discussion

It has been determined that the thermal degradation of poly(alkyl acrylate)s occurs mainly by random chain scissions while that of poly(alkyl methacrylate)s takes place by depolymerization [1–4,14,15]. However, side chain elimination also becomes important when the alkyl chain is sufficiently long [14,15].

The TIC curves, the variation of total ion current as a function of temperature, and the mass spectra at the peak maxima and at the shoulders present in the TIC curves recorded during the pyrolysis of poly(n-butyl acrylate), poly(t-butyl acrylate), and poly(n-butyl methacrylate) are given in Fig. 1. The pyrolysis of PnBMA yielded a single peak in the TIC curve with a maximum at 395 °C and a shoulder at 425 °C (Fig. 1a). In case of PnBA, the TIC curve shows two overlapping peaks, a weak one with a maximum at around 280 °C and an intense one with a maximum at 375 °C and a shoulder at