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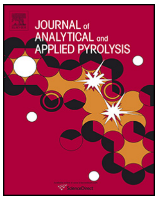

Pyrolysis of of poly(methy methacrylate) copolymers

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ABSTRACT

In this work, thermal degradation of copolymers of poly(methy methacrylate) namely, poly(methyl methacrylate-co-*n*-butyl acrylate), P(MMA-co-*n*Bu), poly(methyl methacrylate-co-*n*-benzyl methacrylate) P(MMA-co-BzMA, and poly(methyl methacrylate-co-isobornyl acrylate), P(MMA-co-IBA) were investigated via direct pyrolysis mass spectrometry. It was determined that whether an available γ-H with respect to the carbonyl groups is present or not determines the thermal degradation mechanisms of polyacrylates and polymethacrylates. Cis elimination reactions become preferential as the first step of thermal decomposition and lead to a multi-step degradation mechanism involving trans-esterification reactions together with elimination of molecules such as alcohols, CO_2, CO and H_2O if γ-Hs to the carbonyl group is present. On the other hand, if there is no γ-H, thermal degradation proceeds by depolymerization yielding mainly the corresponding monomer. Consequently, PMMA and PBzMA decompose by depolymerization mechanisms and in contrast, thermal degradation of PnBA, and PIBA occurs through various reaction pathways involving random chain scissions, cis-elimination and trans-esterification reactions and elimination of CO_2 and CO.

1. Introduction

Polyacrylates and their copolymers, because of their wide applications in paint, paper, adhesive, textile, and leather industries have been studied extensively. Poly(methyl methacrylate-co-butyl acrylate), p(MMA-co-BA) copolymers are extensively used as adhesives and coatings. By combining methyl methacrylate, which can be considered as hard sequences contributing stiffness, with butyl acrylate, as soft sequences copolymer with desired property can be obtained. Polybenzyl methacrylate (PBzMA) is mostly used as curing agent in polymer science. Copolymer of BzMA with MMA is also a valuable end product especially in pharmaceutical industry. Among other several polyacrylates, generally with low glass transition temperature (T_g), poly(isobornyl acrylate) (PIBA) has a number of interesting physical properties such as high glass transition temperature (T_g) (94 °C) and hardness (19.6 kg/mm^2 at 20°).

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. Several studies on thermal degradation of acrylate, methacrylate polymers were appeared in the literature [1–22]. The photooxidative stability of polyacrylates and polymethacrylates has been investigated by Chiantore et al. [13]. They determined that the acrylate units are more reactive toward oxidation, in comparison with the methacrylate ones. With short alkyl side groups chain scissions prevailed over cross-linking reactions both in acrylate and methacrylate samples [13]. In a different study, the photooxidative degradation of poly(alkyl methacrylate)s has been investigated and it has been found that PMMA undergoes slower photooxidation but faster photodegradation than those in higher poly(alkyl methacrylate)s due to the different reactivity of the macroradicals influenced by the different flexibility and mobility of macrochains [14].

The degradation behavior of various high-molecular-weight acrylic polymers namely PMMA, PnBMA, PnBA and poly(lauryl methacrylate) (PLMA) was also investigated under extreme environmental conditions [18]. It was concluded that the general degradation mechanism of studied polymers involves the loss of the ester side groups to form methacrylic acid followed by cross-linking. The conditions required for alcohol production is an important step in polyacrylates degradation mechanism.

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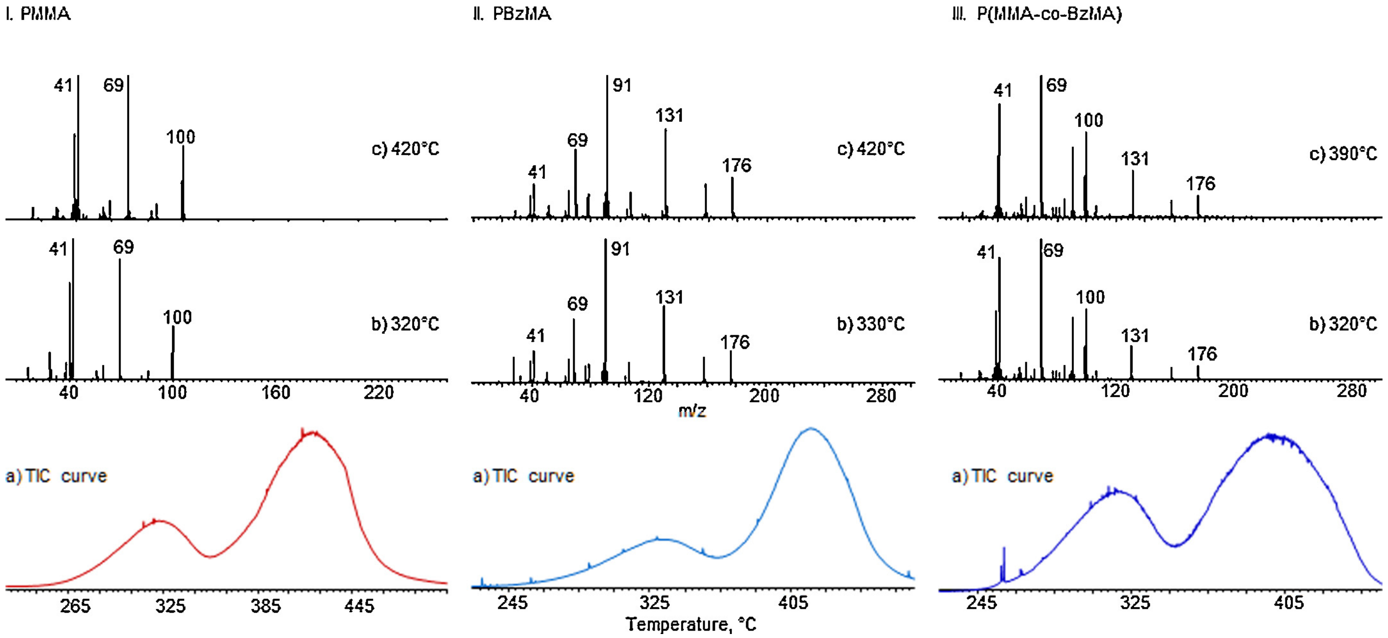

Fig. 1. (a) TIC curves and (b) pyrolysis mass spectra at peak maxima present in the TIC curves recorded during the pyrolysis of I. PMMA, II. PBzMA and III. P(MMA-co-BzMA).

It has also been determined that the degradation behaviors of high-molecular-weight poly(methyl methacrylate) (PMMA), poly(*n*-butyl methacrylate) (PBMA), poly(*n*-butyl acrylate) (PBA), and poly(lauryl methacrylate) (PLMA), under extreme environmental conditions is directly related to the length of the ester side group, with the degradation susceptibility decreasing in the order of PLMA > PBMA/PBA > PMMA [20]. Goikoetxea et al. investigated the mechanisms involved in the formation of *n*-butanol during the synthesis of butyl acrylate containing lattices [21]. The experimental results showed that neither the hydrolysis of butyl acrylate nor of the ester bond in the butyl acrylate segments of the polymer played a major role in the formation of *n*-butanol, which was mainly generated from the polymer backbone, by transfer reactions to polymer chain followed by cyclization.

Thermal decomposition of copolymers of acrylates has also been discussed [23–31]. Konaganti et al. studied the photocatalytic and thermal degradations of PMMA, PBA, and their copolymers of different compositions [26]. The normalized weight loss profiles for the copolymers showed that the thermal stability of the copolymers was increased with the mole percentage of BA in the P(MMA-co-*n*BA) copolymer. Leskovac and coworkers studied the effect of crosslinking agents on the thermal stability of P(MMA-co-*n*BA) and P(S-co-*n*BA) polymers [27]. The results of this study also proved that butyl acrylate sequences increased the thermal stability of copolymers much more in the case of P(MMA-co-*n*BA) copolymers compared to those of the homopolymers, due to the stabilizing effect of BA units.

During the pyrolysis of poly(methyl methacrylate-co-isobornyl methacrylate), P(MMA-co-IBA), intermolecular interactions between PIBA and PMMA chains were detected [29]. Based on evolution of methanol, a trans-esterification reaction between the MMA and acrylic acid units generated by loss of isobornylene from PIBA chains was proposed.

The objective of this study is to investigate systematically the thermal degradation processes of poly(methy methacrylate-co-*n*-butyl acrylate), P(MMA-co-*n*Bu), poly(methy methacrylate-co-*n*-benzyl methacrylate) P(MMA-co-BzMA, and Poly(methyl methacrylate-co-isobornyl acrylate) P(MMA-co-IBA) copolymers via direct pyrolysis mass spectrometry to determine the effects of H-transfer reactions to the carbonyl groups.

2. Experimental

2.1. Chemicals

Methyl methacrylate (MMA, Aldrich), *n*-butyl acrylate (BA, Aldrich), benzyl methacrylate (BzMA, Aldrich) and isobornyl acrylate (IBA, Aldrich) were purified by passing through basic alumina column. Azobis(isobutyronitril) (AIBN) was obtained from Aldrich and used as received.

2.2. Synthesis

PMMA, PBA, PIBA, PBzMA and copolymers (90/10 mol%) were synthesized via bulk polymerization using azobis (isobutyronitril) (AIBN) as an initiator. The same experimental conditions were used in the preparation of PBA, PIBA, PBzMA and copolymers. As a summary, AIBN (0.5 mmol) was dissolved in monomer solutions (0.1 mol) in 25 mL round bottom three-necked flask fitted with a nitrogen inlet and condenser, degased by bubbling nitrogen and stirred at 800 rpm. The polymerization reaction was carried out at 60 °C for 4 h and then at 80 °C for 1 h after the completion of the reaction, the polymer was dissolved in the dichloromethane, precipitated in methanol and dried in high vacuum for 15 h. The characterizations of the samples were done by FTIR and NMR spectrometry techniques. The number, and weight average molecular weights and the polydispersity indexes of the copolymers were determined by gel permeation chromatography (GPC) (Viscotek GPC) using a UV detector (410 model refractive index). Samples were eluted with tetrahydrofuran through a linear ultrastryroge column at a flow rate of 1 mL min^{-1}. The molecular weights were determined relative to PMMA standard. The molecular weights and polydispersity indexes of the copolymers involving two monomers

Table 1
Molecular weights and polydispersity indexes of the copolymers.

Copolymer	Mol%	Mn	Mw	Mw/Mn
P(MMA-co-*n*BA)	87.5 – 12.5	105100	45600	4.3
P(MMA-co-BzMA)	90/10	173500	53300	3.1
P(MMA-co-IBA)	90/10	61100	34600	5.7

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