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Thermal degradation of copolymers based on selected alkyl methacrylates

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Bretsznajder Special Chapter

Abstract The thermal stability and thermal degradation of copolymers based on selected alkyl methacrylates at temperatures between 250 and 400 °C have been studied using pyrolysis–gas chromatography. The type and composition of thermal degradation products gave useful information about the mechanism of pyrolysis of copolymers synthesized by using typical commercially available alkyl methacrylates. It was observed that the main thermal degradation products from alkyl methacrylate copolymers are monomers of alkyl methacrylates using by synthesis. Other pyrolysis by-products formed during thermal degradation were carbon dioxide, carbon monoxide, methane, ethane, methanol, ethanol, and propanol-1.

Keywords Alkyl methacrylate copolymers · Thermal degradation · Pyrolysis · 2-Ethylhexyl methacrylate · Butyl methacrylate · Ethyl methacrylate · Methyl methacrylate

Introduction

Methacrylate copolymers with their excellent physical, chemical, and mechanical properties are widely used in many applications such as raw materials for adhesives, polymeric films, paints, varnishes, and sealants in technical and medical fields. Polymers based on alkyl methacrylates are widely used as construction materials and coatings. Their properties depend particularly on the type of alkyl group in side chain. Chain branching enhances hardness while elongation increases plasticization [1].

Pyrolysis–gas chromatography (Py–GC) is a method, which easily, rapidly and inexpensively characterizes the polymer formulation as polymer or compounded polymeric material [2, 3]. In properly chosen conditions, this method allows to conduct transformation waste into useful products. In case of polymer products, especially polyacrylates and polymethacrylates, it is possible to reproduce monomers which build degradable polymers [4–6]. Using the pyrolysis coupled with gas chromatography also allows identifying investigated material which has significant meaning in case of complaints. The special group of acrylic resins, namely poly(alkyl methacrylates) are attractive and important specialty polymers. They are very interesting for adhesive applications, characterized by excellent compatibility with acrylic and methacrylic polymers and with wide range of other polymers. They can be used especially for modification of aqueous acrylic and methacrylic dispersions. These polymers display several unique properties, such as extremely good weather and aging resistance, non-yellowing properties, low permeability of oxygen, and good plasticizers resistance. Their major advantages are photostability and resistance to hydrolysis [7].

Experimental

Materials

Acrylic copolymers based on alkyl methacrylates were synthesized in ethyl acetate at 77 °C by 50 wt% of polymer content with 1-h dosage time of monomer and 3-h

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Table 1 Molecular weights M_W and M_n and polydispersity of synthesized copolymer containing selected alkyl methacrylates

AIBN/wt%	Viscosity/Pa s	$\bar{M}_W$/Da	$\bar{M}_n$/Da	$P_d = \frac{\bar{M}_W}{\bar{M}_n}$
0.1	11.8	657,000	228,000	2.88
0.2	9.3	552,000	177,000	3.12
0.3	5.4	398,000	113,000	3.52

post-reaction using 40 wt% of 2-ethylhexyl methacrylate (2-EHMA), 30 wt% of butyl methacrylate (BMA), 20 wt% of ethyl methacrylate (EMA), and 10 wt% of methyl methacrylate (MMA) in the presence of 0.1, 0.2, and 0.3 wt% of radical thermal initiator 2,2′-azo-bis-diisobutyronitrile (AIBN) according to polymer content. The different concentration of AIBN allows to variation of viscosity and molecular weight of synthesized copolymers. All raw materials were purchased from BASF, Germany.

The synthesized copolymers based on selected alkyl methacrylates were characterized by viscosities measured at room temperature using a viscosimeter Rheomat RM (Rheometric Scientific) with nr 3 spindle and by weight average molecular weights ($\bar{M}_W$), number average molecular weights ($\bar{M}_n$), and polydispersities (P_d) (Table 1). Molecular weight was determined with the use of liquid chromatography LaChrom: RI Detector Li-7490 and LaChrom UV Detector L-7400 Merck Hitachi supplied with PLgel 10^6 Helwett-Packard column.

The synthesized solvent-borne copolymers were dried for 10 min at 110 °C in drying canal and after drying as dry solvent-free polymer films were tested on thermal stability and further pyrolyzed. The formed pyrolysis products were investigated using gas chromatography.

Thermal stability

Copolymer stability was assessed by thermogravimetry (TG) using model 2950 TGA unit interfaced with the TA Instruments Thermal Analyst 2100 control unit from TA Instruments Inc. The sample about 5 mg was contained in a platinum sample pan and the TG cell was swept with nitrogen at 50 mL min^{-1} during degradation runs. The temperature was ramped at 5 °C min^{-1} in the area between 200 and 400 °C.

Degradation process

The quantitative and qualitative analyses were conducted by using the following gas chromatography methods:

The determination of liquid products were conducted with an external standard method and following analytical conditions: gas chromatograph ThermoScientific GC8000$^{\text{Top}}$, capillary column—RESTEK RTX-5 30 m × 0.53 mm, 1.5 μm film, carrier gas—He 5 $\text{cm}^3\ \text{min}^{-1}$, detector temperature (FID)—300 °C, injector temperature—280 °C (split 1:2), oven-temperature program—45 °C (4 min) to 420 °C at 10 °C min^{-1}.

The determination of gaseous products were conducted with an external standard method and following analytical conditions: gas chromatograph ThermoScientific TraceUltra micropacked column—ShinCarbon ST 100/120, 1 m, 0.95 mm, carrier gas—He 8 $\text{cm}^3\ \text{min}^{-1}$, detector temperature (TCD)—200 °C, injector temperature—100 °C, oven-temperature program—45 °C (10 min) to 250 °C at 10 °C min^{-1}.

Results and discussion

The stability of the synthesized copolymer was determined by TG.

Figure 1 illustrates a comparison of the thermal degradation characteristics of synthesized copolymers with different molecular weights.

As can readily be seen, the rate of initiation of degradation is much greater for the acrylic copolymers synthesized from 2-EHMA, BMA, EMA, and MMA with greater molecular weight than for copolymers with lower molecular weight (Fig. 1).

The synthesis of copolymers based on selected alkyl methacrylates in the presence of 0.1, 0.2, and 0.3 wt% of radical thermal initiator AIBN allows to variation of viscosity and molecular weight of synthesized copolymers. The influence of AIBN amount on the molecular weight of synthesized solvent-borne methacrylic copolymers is illustrated in Table 1. The relatively high concentration of AIBN contributes to a greater possibility of free radical transfer during polymerization reaction by which de facto

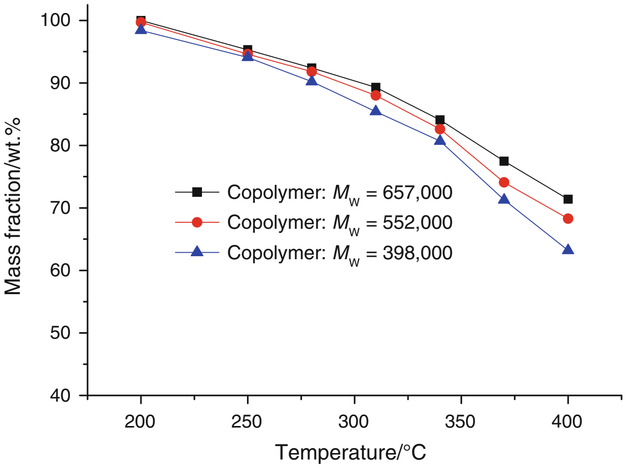

Fig. 1 Thermal stability of acrylic copolymers as a function of their molecular weight M_W

Table 2 Composition of breakdown products during thermal degradation of acrylic copolymer

Pyrolysis products	Concentration of breakdown products/wt%					
Pyrolysis temperature/°C:	250	280	310	340	370	400
Methyl methacrylate	99.8	99.7	99.6	98.1	97.4	96.6
Ethyl methacrylate	99.6	99.2	98.3	97.0	95.3	94.1
Butyl methacrylate	99.1	98.2	97.2	95.9	94.1	92.0
2-Ethylhexyl methacrylate	96.8	95.3	94.2	93.1	90.7	88.7
Carbon monoxide	–	0.2	0.7	0.9	1.2	1.6
Carbon dioxide	–	0.2	0.6	0.8	1.0	1.2
Methane	–	–	0.1	0.3	0.5	0.8
Ethane	–	–	0.1	0.1	0.1	0.1
Methanol	–	–	0.1	0.1	0.1	0.1
Ethanol	–	0.1	0.5	0.8	1.2	1.7
Propanol	–	0.1	0.2	0.5	0.9	1.4

the molecular weights M_W and M_n of solvent-borne methacrylic copolymers decreases.

The thermal degradation products from copolymer containing the polymer structure segments of 2-EHMA, BMA, EMA, and MMA in temperatures between 250 and 400 °C are summarized in Table 2, which also shows the concentration of the breakdown products as a function of temperature range. The thermal degradation investigations were performed for acrylic copolymer with highest molecular weight M_W of 657,000. At lower temperatures, the polymers degrade nearly completely to the monomers alkyl methacrylates, alcohols and gases, and carbon dioxide, carbon monoxide, methane, and later ethane appear only in small quantities. At higher temperatures, the copolymer concentration based on alkyl methacrylates decreases slowly, while the gas component content simultaneously increases.

It is illustrated in Table 2, between 250 and 400 °C, the concentration of methacrylate monomers drops from 99.8 to 96.6 wt% for MMA, from 99.6 to 94.1 wt% for ethyl acrylate, from 99.1 to 92.0 wt% for BMA and from 96.8 wt% to 88.7 wt% for 2-EHMA in thermal degradation by-products. The concentrations of gases and alcohols are very low and continuously increase from 0.6 wt% at 250 °C to 6.9 wt% at 400 °C. The concentration of thermal degradation products as a function of pyrolysis time are presented in Fig. 2.

The major gaseous products are carbon monoxide, carbon dioxide, methane, and ethane. A small concentration of alcohols like methanol, ethanol, and propanol-1 was observed too. It was confirmed for each copolymers, based on selected alkyl methacrylate, that the corresponding methacrylate, such as MMA, EMA, BMA, and 2-EHMA are the genuine thermal degradation products, and they were only present in investigated pyrolysates. In discussing the thermal degradation process of acrylic copolymers based on alkyl methacrylates, it should be emphasized that it is a depolymerization process. The process of diffusion of degradation products throughout the acrylic polymers also plays an important role. The most important of these factors are the degradation conditions, especially the temperature of pyrolysis. It has not been observed the formation of typical breakdown products typically for poly(alkyl acrylates), such as alkenes, long chain alcohols and acrylate monomers.

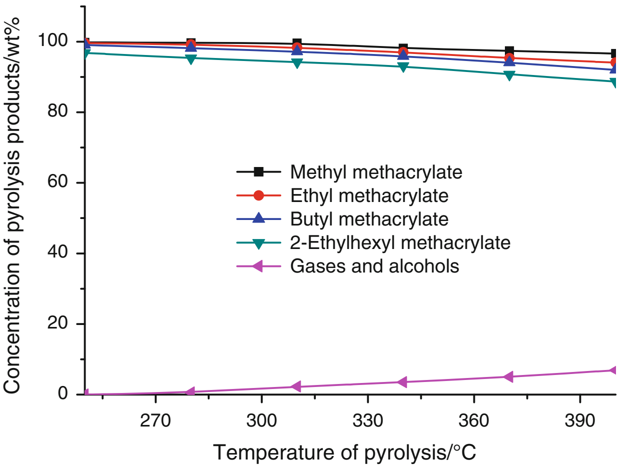

Fig. 2 Pyrolysis products during the pyrolysis of acrylic copolymer based on selected methyl methacrylates

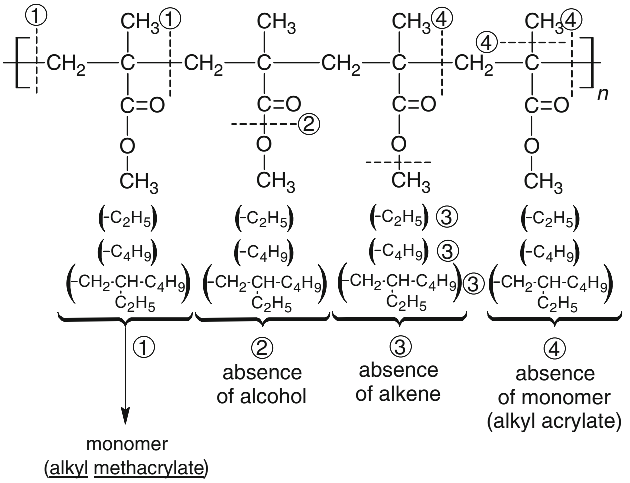

Fig. 3 Thermal degradation mechanism of poly(alkyl methacrylates)

The general thermal degradation mechanism of acrylic copolymers based on alkyl methacrylates includes random main-chain scission and side chain reactions. As a result of random main-chain scission, monomers are formed according to Fig. 3.

The principal degradation products of poly(alkyl methacrylates) are accordingly monomers used in polymerization process, and in the temperature range of interest, the amount of the monomer formed (only methacrylates) according to process ① is very much dependent upon the pyrolysis temperature. The formation of energetically less favorable primary carbon radicals leads to methacrylate evolution.

From the quantitative results, it is possible to observe the effect of monomer yields, depending on the number of carbon atoms in the alkyl side chain. The concentrations of monomers for short alkyl side chain (methyl, ethyl) were higher than for monomers from long side chain (butyl, 2-ethylhexyl). The longer the alkyl side chain in the poly(alkyl methacrylates), the lesser the monomers were formed during the pyrolysis. During cracking effect, especially at higher temperatures, gaseous products and mixture of low molecular alcohols are formed.

Conclusions

This work gives the full all-round results of thermal degradation of poly(alkyl methacrylates) in the wide range of high temperatures and suggests simple degradation mechanism providing a satisfactory explanation for the formation of major destruction products, namely alkyl methacrylates, such as methyl methacrylate, EMA, BMA, and 2-EHMA. The general mechanism of poly(alkyl methacrylates) thermal degradation includes random main-chain scission reactions. Poly(alkyl methacrylates) produce monomers as the predominant degradation products in all investigated pyrolysis condition between 250 and 400 °C. This excellent process can be applied for material recycling of methacrylic polymers waste for recovery of methacrylate monomers.

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