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Thermal degradation of poly(alkyl methacrylates)

Zbigniew Czech · Robert Pełech

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Abstract The thermal degradation of selected poly(alkyl methacrylates) at temperatures between 300 and 800 °C was investigated by pyrolysis gas chromatography. Quantitative characterization of the pyrolysis products yields insights into the mechanism for thermal degradation of poly(alkyl methacrylates) under these conditions. Unsaturated monomeric alkyl methacrylates, carbon dioxide, carbon monoxide, methane, ethane, methanol, ethanol, and propanol were formed during thermal degradation of poly(alkyl methacrylates).

Keywords Poly(alkyl methacrylates) · Solvent-borne polymerization · Thermal degradation · Pyrolysis · Breakdown products

Introduction

Organic polymeric materials are widely used as coatings in a variety of markets and applications, primarily to improve surface properties, appearance, and performance. As these applications become more sophisticated, the multivariate nature of the coating and decreased dimensions often produce layers of polymers with different properties. In addition, the viscoelasticity of most polymers leads to a performance that depends markedly on time and temperature [1]. Acrylic resins are used as a primary binder in a wide variety of industrial coatings. These polymers have many excellent properties, particularly exterior durability, but their use has declined because large quantities of solvent are required to sufficiently reduce viscosity for application [2].

A special group of acrylic resins, poly(alkyl methacrylates), are attractive and important specialty polymers. They are excellent for adhesive applications, characterized by good compatibility with acrylic and methacrylic polymers as well as a wide range of other polymers. They can be used for modification of aqueous acrylic and methacrylic dispersions. These polymers display several unique properties, such as weather and aging resistance, non-yellowing properties, low permeability to oxygen, and good plasticizer resistance. Their major advantages are photostability and resistance to hydrolysis [3].

The thermal behavior of acrylics and acrylic copolymers has been the target of some reports [4–9]. Investigations of the thermal behavior and thermal decomposition process of poly(alkyl methacrylates) are relevant to studies of the material deterioration during high-temperature processing. For this purpose, the thermal properties and decomposition of poly(alkyl methacrylates) have been investigated by pyrolysis gas chromatography (PGC) techniques. PGC has been used extensively to determine chemical structure resistance as a function of increasing temperature, especially during thermal degradation [10]. Thermal decomposition of methacrylic polymers is relevant to the deterioration of polymer properties during high-temperature processing [11]. The use of pyrolysis-based analytical techniques and pyrolytic methods to recover chemical feedstock from polymer wastes are also of interest.

Z. Czech (✉) · R. Pełech
Institute of Chemical Organic Technology, West Pomeranian University of Technology, Szczecin, Pulaskiego 10, 70-322 Szczecin, Poland
e-mail: psa_czech@wp.pl

Experimental

Materials

The solvent-borne polymerization of methyl acrylate, ethyl acrylate, butyl acrylate, and 2-ethylhexyl acrylate (monomers were purchased from BASF, Germany) was conducted in ethyl acetate at 77 °C under nitrogen atmosphere in the presence of 0.1 wt% 2,2′-azo-bis-diisobutyronitrile (AIBN) (ChemCycle, Germany). AIBN is a thermal initiator that starts radical polymerization during a 1-h dosage time, and polymerization is continued during a 3-h post-reaction with 50 wt% polymer content reaction conditions. The synthesized methacrylic homopolymers were characterized by weight average molecular weight ($\overline{M}_{w}$), number average molecular weight ($\overline{M}_{n}$), and polydispersity (P_{d}) (Table 1).

The solvent-borne poly(alkyl methacrylates) were dried for 10 min at 110 °C in a drying channel and, after drying, the polymer films were pyrolyzed. The pyrolysis products were characterized by gas chromatography.

Degradation process

Quantitative and qualitative analysis was conducted by the following gas chromatography methods:

The characterization of liquid products was conducted using an external standard method under the following analytical conditions: ThermoScientific GC8000^{Top} gas chromatograph with a RESTEK RTX-5 capillary column, 30 m × 0.53 mm; 1.5 µm film; He carrier gas, 5 cm^3 min^{-1}; 300 °C detector temperature (FID); 280 °C injector temperature (split 1:2); oven temperature program, 45 °C (4 min) to 320 °C at 10°C min^{-1}.

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

Table 1 Molecular weights of synthesized methacrylic homopolymers

Monomer	$\overline{M}_{w}$ (Dalton)	$\overline{M}_{n}$ (Dalton)	$P_{d}=\frac{\overline{M}_{w}}{\overline{M}_{n}}$
Methyl methacrylate	875,600	280,600	3.12
Ethyl methacrylate	798,000	212,800	3.75
Butyl methacrylate	723,800	168,000	4.31
2-Ethylhexyl methacrylate	643,700	141,500	4.55

Results and discussion

The breakdown products from poly(alkyl methacrylates) between 300 and 800 °C are summarized in Tables 2, 3, 4, and 5, which also show the concentration of breakdown

Table 2 Composition of breakdown products from investigated poly(methyl methacrylate)

Pyrolysis products	Pyrolysis temperature/°C					
	300	400	500	600	700	800
	Weight % of original methacrylic polymer					
Carbon dioxide	–	0.7	1.0	3.3	20.3	21.4
Carbon monoxide	–	0.7	1.0	3.6	19.6	20.1
Methane	–	0.3	1.6	3.3	15.9	16.7
Ethane	–	–	0.3	0.6	0.9	1.5
Methyl methacrylate	99.7	96.6	92.1	80.3	20.8	11.8
Methanol	–	–	0.4	0.6	2.1	3.4
Ethanol	–	0.7	1.0	2.1	6.2	6.1
Propanol	–	0.6	1.1	2.3	5.9	5.8

Table 3 Composition of breakdown products from investigated poly(ethyl methacrylate)

Pyrolysis products	Pyrolysis temperature/°C					
	300	400	500	600	700	800
	Weight % of original methacrylic polymer					
Carbon dioxide	0.4	0.8	1.4	6.0	22.6	23.1
Carbon monoxide	0.6	1.2	1.6	5.4	22.2	22.0
Methane	–	0.7	2.2	4.0	16.2	17.2
Ethane	–	–	0.3	0.6	0.8	1.6
Ethyl methacrylate	98.3	94.1	86.0	71.2	13.6	8.6
Methanol	–	–	0.3	0.8	2.6	3.3
Ethanol	0.3	1.5	2.2	4.0	6.0	6.0
Propanol	–	1.3	2.0	4.0	5.8	6.0

Table 4 Composition of breakdown products from investigated poly(butyl methacrylate)

Pyrolysis products	Pyrolysis temperature/°C					
	300	400	500	600	700	800
	Weight % of original methacrylic polymer					
Carbon dioxide	0.5	1.2	4.0	7.8	23.5	24.5
Carbon monoxide	0.7	1.8	4.3	6.9	22.5	22.5
Methane	–	0.8	3.0	5.8	20.5	20.5
Ethane	–	–	0.5	0.8	1.0	2.0
Butyl methacrylate	97.5	92.0	80.9	63.8	7.7	–
Methanol	–	–	0.5	1.0	3.0	3.5
Ethanol	0.5	1.8	3.0	5.0	7.0	8.0
Propanol	0.4	1.8	2.8	5.0	6.0	6.5

Table 5 Composition of breakdown products from investigated poly(2-ethylhexyl methacrylate)

Pyrolysis products	Pyrolysis temperature/°C					
	300	400	500	600	700	800
	Weight % of original methacrylic polymer					
Carbon dioxide	1.5	2.1	6.2	8.6	24.7	25.6
Carbon monoxide	1.7	2.4	6.5	8.2	23.0	23.1
Methane	0.4	1.2	4.3	7.1	20.3	20.5
Ethane	–	0.3	0.8	0.9	1.5	2.2
2-Ethylhexyl methacrylate	94.7	88.7	70.4	58.7	5.2	–
Methanol	–	–	0.8	1.7	3.7	4.1
Ethanol	1.1	2.8	3.7	5.3	6.4	8.5
Propanol	0.5	1.9	3.1	5.2	5.9	6.9

products in a different temperature range. At lower temperatures, the polymers degrade nearly completely to the monomeric alkyl methacrylates, alcohols; gases (carbon dioxide, carbon monoxide, methane, and later, and ethane) appear only in small quantities. At higher temperatures, the alkyl methacrylate concentration decreases slowly, whereas the gas content concomitantly increases. Between 600 and 700 °C, however, the quantities of alkyl methacrylates drop sharply from 60 to 5% (2-ethylhexyl methacrylate) and from 80 to 20% (methyl methacrylate). At the same time, the concentration of gases increases sharply (Figs. 1, 2, 3, 4). The alcohol content shows a nearly continuous increase up to 600 °C; above 800 °C, however, alcohols completely disappear. It is likely that the pyrolysis products above 900 °C are composed only of gases. In order to illustrate this effect, Figs. 1, 2, 3, and 4 plot the gas quantities (monomeric alkyl methacrylate and alcohols) as a function of temperature.

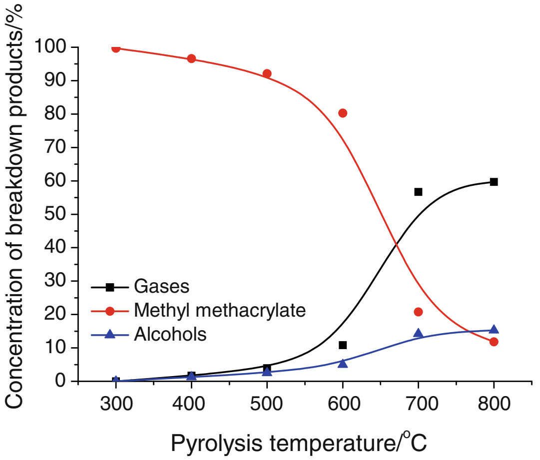

Fig. 1 Breakdown products during the pyrolysis of poly(methyl methacrylate)

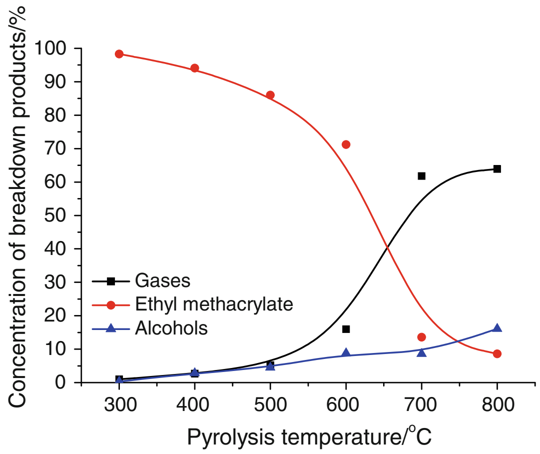

Fig. 2 Breakdown products during the pyrolysis of poly(ethyl methacrylate)

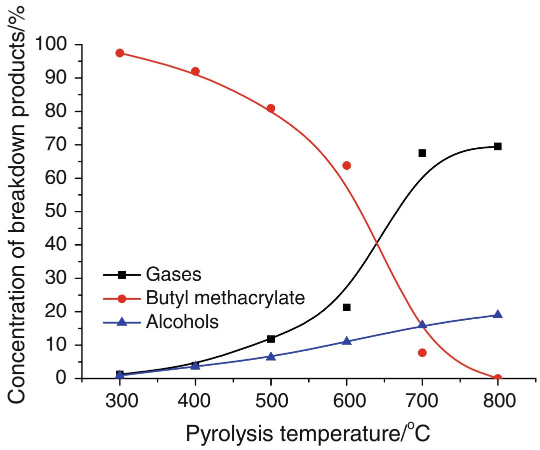

Fig. 3 Breakdown products during the pyrolysis of poly(butyl methacrylate)

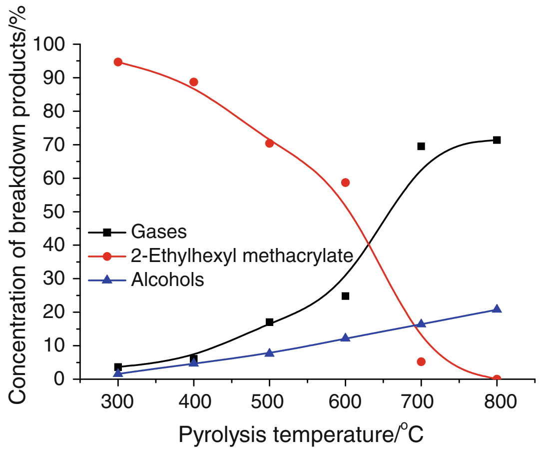

Fig. 4 Breakdown products during the pyrolysis of poly(2-ethylhexyl methacrylate)

In discussing the process of thermal degradation of poly(alkyl methacrylates), it should be emphasized that the process is complex and multistage. Degradation proceeds by a series of both sequential and simultaneous initiation, depolymerization, scission (of the side and main chains of the macromolecules), chain termination, and recombination reactions. The diffusion of degradation products throughout the sample and the degradation conditions, which include temperature, heating rate, and the atmosphere in which the process occurs, play important roles. Figures 5, 6, and 7 show the influence of pyrolysis temperature on the major thermal breakdown products, such as gases (Fig. 5), monomeric alkyl methacrylates (Fig. 6), and alcohols (Fig. 7) during the thermal degradation of poly(alkyl methacrylates). The major breakdown products from thermal degradation of poly(alkyl methacrylates) are carbon dioxide, carbon monoxide, methane, and ethane gases, monomeric alkyl acrylates, and alcohol mixtures containing methanol, ethanol, and propanol (Tables 2, 3, 4, 5). The typical breakdown products of poly(alkyl acrylates), such as alkenes, alcohols, and acrylates, were not observed. The influence of temperature on the product distribution is apparent, and high pyrolysis temperatures lead to a higher proportion of products typical of thermal cracking reactions (carbon dioxide, carbon monoxide, methane, ethane, methanol, ethanol, and propanol). The gas and alcohol yields increase with increasing pyrolysis temperatures because decarboxylation of the polymer chain accelerates at high temperatures.

The evolution of the major breakdown products during the thermal degradation of poly(alkyl methacrylates), namely the respective monomers of alkyl methacrylates, is illustrated in Fig. 8. The principal degradation products of poly(alkyl methacrylates) are the monomers used in the polymerization process. In the temperature range of interest, the quantity of monomers formed (methacrylates only)

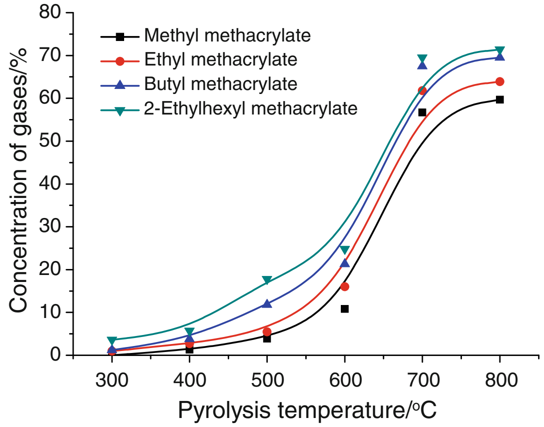

Fig. 5 Influence of pyrolysis temperature on gases products yield during degradation of poly(alkyl methacrylates)

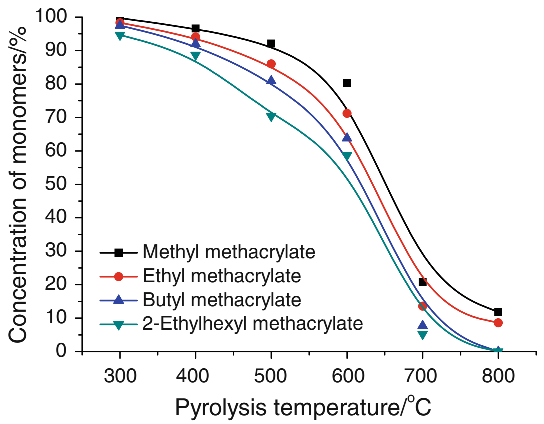

Fig. 6 Influence of pyrolysis temperature on monomers yield during degradation of poly(alkyl methacrylates)

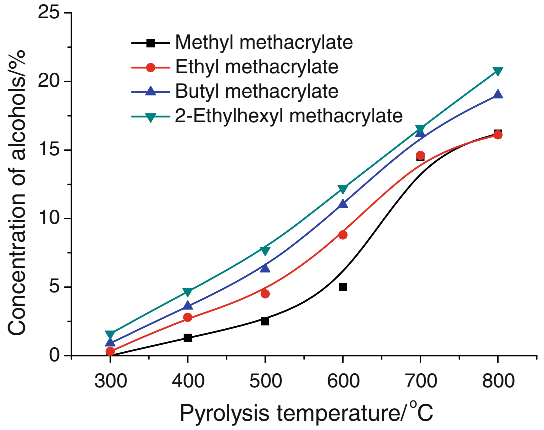

Fig. 7 Influence of pyrolysis temperature on alcohols yield during degradation of poly(alkyl methacrylates)

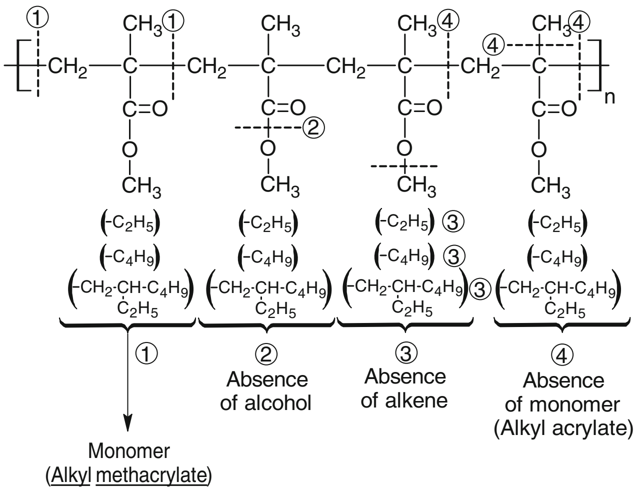

Fig. 8 Thermal degradation mechanism of poly(alkyl methacrylates)

according to process ① depends strongly upon the pyrolysis temperature. The concentration of monomers was measured at different pyrolysis temperatures between 300 and 800 °C. Figure 6, the result of the present investigations, clearly shows that this concentration correlates directly with the type of polymer degraded and the pyrolysis temperature. These results quantify the various monomer yields, which depend on the number of carbon atoms in the alkyl side chain. The concentrations of monomers with short alkyl side chains (methyl and ethyl) were higher than for monomers with long side chains (butyl and 2-ethylhexyl). Longer alkyl side chains in poly(alkyl methacrylates) corresponded to fewer monomers formed during pyrolysis. The mechanism of thermal degradation, presented in Fig. 8, supports the absence of alkenes, the presence of alcohols, and monomeric alkyl acrylates, which are excluded in the pyrolysis mechanisms ②, ③, and ④. During cracking reactions, especially at higher temperatures, gaseous products and mixtures of low molecular weight alcohols are formed.

Conclusions

The investigations presented here give a thorough description of the thermal degradation of poly(alkyl methacrylates) at a wide range of high temperatures. A simple degradation mechanism is suggested, providing a satisfactory explanation for the formation of the major breakdown products of alkyl methacrylates, such as methyl methacrylate, ethyl methacrylate, butyl methacrylate, and 2-ethylhexyl methacrylate. Poly(alkyl methacrylates) undergo a thermal degradation process at high temperatures that includes main chain scission. The concurrent reactions under the conditions investigated do not give rise to the formation of alkenes, acrylates, or alcohols. An increase in pyrolysis temperature leads to higher yields of products derived from the main and side chains at cracking temperatures, such as carbon dioxide, carbon monoxide, methane, ethane, or low molecular weight alcohols. During thermal degradation, poly(alkyl methacrylates) produce monomer methacrylates as the predominant breakdown product in all tested pyrolysis conditions.

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