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Pyrolysis of methacrylic polymers

The methacrylic polymers based on poly(alkyl methacrylates) are important specialty polymers. They are very interesting for adhesive applications, characterized by excellent compatibility with acrylic, methacrylic and with wide range of other polymers. They can be used especially for modification of aqueous acrylic and methacrylic dispersions, and for manufacturing of polymeric films. 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. The thermal behavior of methacrylic copolymers has been the target of some reports. During the pyrolysis of methacrylic polymers were observed such kinds of products, as alkyl methacrylates, carbon dioxide, carbon monoxide, methane, ethane, methanol, ethanol and propanol.

Key words: poly(alkyl methacrylates), pyrolysis, pyrolysis products

Piroliza polimerów metakrylanowych

Polimery metakrylanowe na podstawie poli(alkilometakrylanów) stanowią interesującą i ważną grupę polimerów specjalnych. Dzięki korzystnym właściwościom, a zwłaszcza kompatybilności z wieloma rodzajami polimerów, znajdują one zastosowanie w produkcji klejów jako wodne dyspersje akrylanowe oraz metakrylanowe. Są również szeroko stosowane do produkcji folii polimerowych, charakteryzujących się bardzo dobrą odpornością na warunki zewnętrzne, odpornością na starzenie, małą penetracją tlenu, brakiem żółknięcia oraz odpornością na niszczące działanie plastyfikatora. Przedmiotem badań był przebieg termicznej degradacji kopolimerów metakrylanowych. W trakcie pirolizy poli(alkilometakrylanów) zaobserwowano tworzenie się takich produktów, jak metakrylany alkilowe, dwutlenek węgla, tlenek węgla, metan, etan, metanol, etanol oraz propanol.

Słowa kluczowe: poli(alkilometakrylany), piroliza, produkty pirolizy

I. Introduction

Pyrolysis has been used extensively over the last 20–30 years as an analytical technique in which large molecules are degraded into smaller volatiles species using only thermal energy. The ultimate objective of analytical pyrolysis is to use the chromatographic information of pyrolysis products to determine the composition or structure of the original sample. The complexity of polymeric materials can vary extensively and they can be very challenging to analyze. Pyrolysis, combined with modern analytical methods, such as gas chromatography and/or mass spectrometry (Py–GC/MS) has become a quick, convenient and powerful tool for characterizing polymers from non-volatile, complex heterogeneous samples. Degradation results from free radical reactions initiated by bond breaking within the molecules; the bond that is more easily broken will be favored. Thermal and environmental conditions, such as temperature and additional reactants, can affect both the extent and route of degradation of a polymeric material and the nature (physical and chemical) and quantity of molecular species generated by pyrolysis. Molecular degradation of a sample will occur as soon as the temperature is high enough to initiate bond breaking, but at this point will

not necessarily yield much useful product. With much higher temperatures, other bonds will break simultaneously, creating very small and non-specific free radicals. Generally, the higher the temperature, the smaller the radicals and molecules produced. The optimum pyrolysis temperature, which will be different for every polymer, is the point at which degradation produces a wide array of chemically useful products [1].

Investigation of thermal behavior and thermal decomposition of homopolymers or copolymers based on poly(alkyl methacrylates) are relevant to the study of deterioration of materials properties during high-temperature processing. For this purpose, the thermal properties and decomposition of copolymers based on poly(alkyl

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methacrylates) have been investigated by pyrolysis–gas chromatography (PGC) techniques. PGC has been used extensively to determine the chemical structure resistance as a function of temperature increasing, especially by thermal degradation. Thermal decomposition of methacrylic polymers is relevant to deterioration of polymers properties during high-temperature processing [2-6]. The use of pyrolysis-based analytical techniques and pyrolytic methods to recover chemical feedstock from polymer waste are also of interest.

2. Experimental

2.1. Synthesis of poly(alkyl methacrylates)

The polymerization trials of 95 wt.% methyl acrylate, ethyl acrylate, butyl acrylate and 2-ethylhexyl acrylate as copolymers with 5 wt.% acrylic acid were conducted as solvent-borne polymers in organic solvent ethyl acetate at 77°C in nitrogen atmosphere in the presence of 0.1 wt.% 2,2'-azo-bis-diisobutyronitrile (AIBN) according to polymerized monomers as a thermal initiator to start radical polymerization conducted by 1 h dosage time of monomers mixture by 3 h post-reaction and with 50 wt.% polymer content.

2.2. Measurement of viscosity and molecular weight

The viscosity of the investigated solvent-borne methacrylic polymers was determined with a Rheomat RM 189 from Rheometric Scientific, with spindle No 3 at 23°C.

The molecular weight studies were performed with a liquid chromatograph LaChrom system: RI Detector L-7490 and LaChrom UV Detector L-7400 from Merck Hitachi, equipped with a PLgel 10⁶ A column from Hewlett Pacard.

2.3. Evaluation of residue monomers

The amount of solid materials was found according to DIN EN 12092, the residual of monomers were measured with gas chromatograph Unicam 610, J&W DB-1 column, FID detector and integrator Unicam 4815.

2.4. Preparation of polymer films

The synthesized solvent-borne poly(alkyl methacrylates) were coated on adhesive silicon paper, dried 10 min at 110°C in drying canal and after drying pyrolyzed as free polymer films.

2.5. Pyrolysis of prepared polymers films

The quantitative and qualitative pyrolysis were conducted by using of 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^{Top}, capillary column – RESTEK RTX-5 30 m × 0.53 mm, 1.5 μm film, carrier gas – He 5 cm³/min, detector temperature (FID) – 300°C, injector temperature – 280°C (split 1:2), oven–temperature program – 45°C (4 min) to 320°C at 10°C/min.

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 cm³/min, detector temperature (TCD) – 200°C, injector temperature – 100°C, oven–temperature program – 45°C (10 min) to 250°C at 10°C/min.

3. Results and discussion

3.1. Viscosity, molecular weight and residue monomers of synthesized methacrylic polymers

The synthesized methacrylic copolymers were characterized by viscosity, weight average molecular weight (\bar{M}_w), number average molecular weight (\bar{M}_n), and polydispersity (P_d). The mentioned properties were presented in Table 1.

As results of copolymerization of selected alkyl methacrylates, such as methyl methacrylate (MMA), ethyl methacrylate (EMA), butyl methacrylate (BMA)

Table 1. Viscosity and molecular weight and of synthesized methacrylic copolymers

Tabela 1. Lepkość i ciężar cząsteczkowy zsyntezowanych polimerów metakrylanowych

| Copolymer | Viscosity [Pa·s] | \bar{M}_w | \bar{M}_n | $P_d = \bar{M}_w/\bar{M}_n$ |
|--|------------------|-------------|-------------|-----------------------------|
| methyl methacrylate/acrylic acid | 8.8 | 875 600 | 280 600 | 3.12 |
| ethyl methacrylate/acrylic acid | 8.0 | 798 000 | 212 800 | 3.75 |
| butyl methacrylate/acrylic acid | 7.4 | 723 800 | 168 000 | 4.31 |
| 2-ethylhexyl methacrylate/acrylic acid | 6.5 | 643 700 | 141 500 | 4.55 |

and 2-ethylhexyl methacrylate (2-EHMA) with acrylic acid were received copolymers characterized by low concentration of residue free monomers < 0.3 wt.%, exactly in the case of MMA (0.09 wt.%), EMA (0.12 wt.%), BMA (0.19 wt.%) and for 2-EHMA (0.23 wt.%). As shown in Table 1 the increasing of the length of alkyl-chain in methacrylates structure decrease the viscosity and both measured molecular weights of synthesized copolymers, and increase their polydispersity.

3.2. Thermal degradation products received during pyrolysis of investigated methacrylic polymers

The breakdown products from selected copolymers based on poly(alkyl methacrylates) between 300°C and 800°C are summarized in Table 2 (copolymer based on poly(methyl methacrylate)) and Table 3 (copolymer based on poly(2-ethylhexyl methacrylate)), which also show the concentration of the breakdown products but now in a different temperature range. At lower temperatures, the polymers degradation (in this concrete case depolymerization) nearly completely to the monomers alkyl methacrylates, alcohols and gases (carbon dioxide, carbon monoxide, methane and later ethane) appear only in small quantities. At higher temperatures, the alkyl methacrylates concentration decreases slowly, while the gas component content simultaneously increases.

Table 2. Composition of breakdown products from investigated copolymer based on poly(methyl methacrylate)
Tabela 2. Skład produktów otrzymanych w wyniku pirolizy kopolimeru na podstawie poli(metakrylanu metylu)

| Pyrolysis products | Pyrolysis temperature [°C] | | | | | |
|---------------------|--|------|------|------|------|------|
| | 300 | 400 | 500 | 600 | 700 | 800 |
| | wt.% of original methacrylic copolymer | | | | | |
| 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 |

The obtained results reveals that between 600°C and 700°C, however, the alkyl methacrylates amount drops sharply from about 60% (2-ethylhexyl methacrylate) and 80% (methyl methacrylate) to about accordingly 5-20%. At the same time the concentration of gases increases very sharply (Figs. 1-4). The content of

alcohols shows a nearly continuous increase up to 600°C; above 800°C; however, they completely disappear. Probable, the pyrolysis products above 900°C are composed only of gases.

Table 3. Composition of breakdown products from investigated copolymer based on poly(2-ethylhexyl methacrylate)

Tabela 3. Skład produktów otrzymanych w wyniku pirolizy kopolimeru na podstawie poli(metakrylanu 2-etyloheksylu)

| Pyrolysis products | Pyrolysis temperature [°C] | | | | | |
|---------------------------|--|------|------|------|------|------|
| | 300 | 400 | 500 | 600 | 700 | 800 |
| | wt.% of original methacrylic copolymer | | | | | |
| 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 |

To illustrate this effect, in Figures 1-4 the amount of gases, monomer alkyl methacrylate and alcohols is plotted as a function of temperature.

In discussing the process thermal degradation of copolymers based on poly(alkyl methacrylates), it should be emphasized that it is a complex multistage process. It consists of a series of consecutive and simultaneous reactions of initiation, depolymerization, scission of the side- and the chain of macromolecules, chain termina-

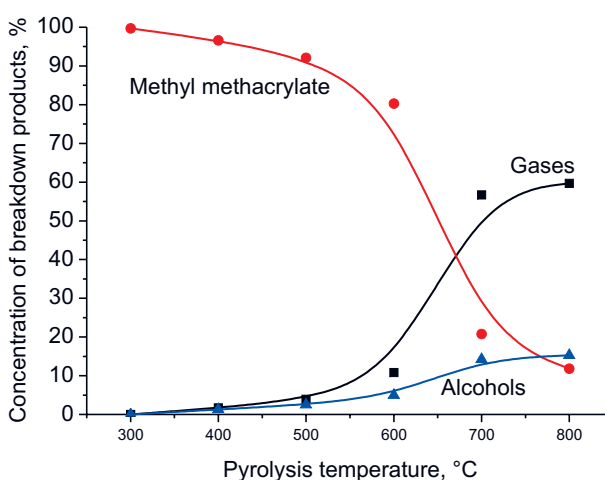


Figure 1. Breakdown products during the pyrolysis of copolymer based on poly(methyl methacrylate)

Rysunek 1. Pirolityczne produkty degradacji termicznej kopolimeru na podstawie poli(metakrylanu metylu)

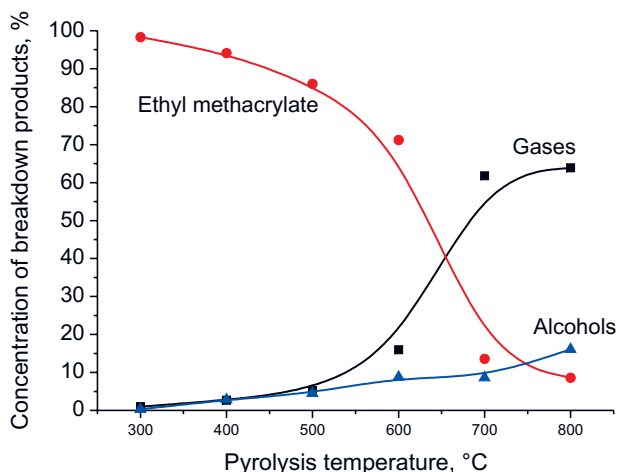


Figure 2. Breakdown products during the pyrolysis of copolymer based on poly(ethyl methacrylate)
Rysunek 2. Pirolityczne produkty degradacji termicznej kopolimeru na podstawie poli(metakrylanu etylu)

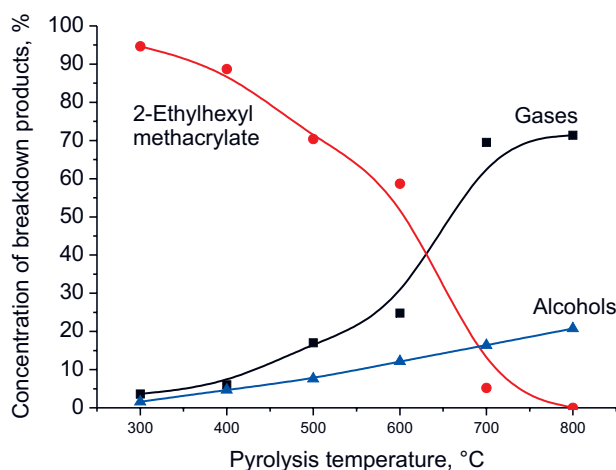


Figure 4. Breakdown products during the pyrolysis of copolymer based on poly(2-ethylhexyl methacrylate)
Rysunek 4. Pirolityczne produkty degradacji termicznej kopolimeru na podstawie poli(metakrylanu 2-etyloheksylu)

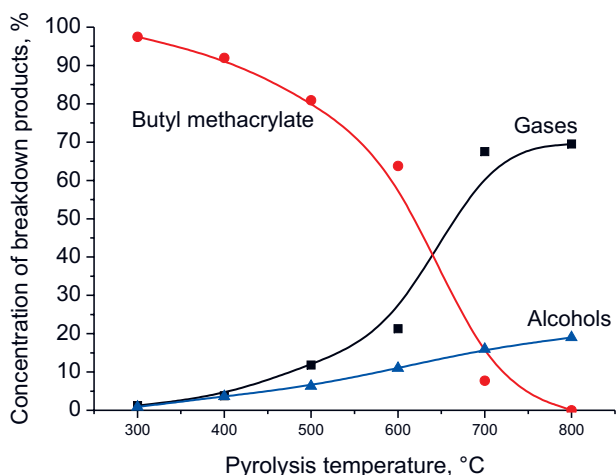


Figure 3. Breakdown products during the pyrolysis of copolymer based on poly(butyl methacrylate)
Rysunek 3. Pirolityczne produkty degradacji termicznej kopolimeru na podstawie poli(metakrylanu butylu)

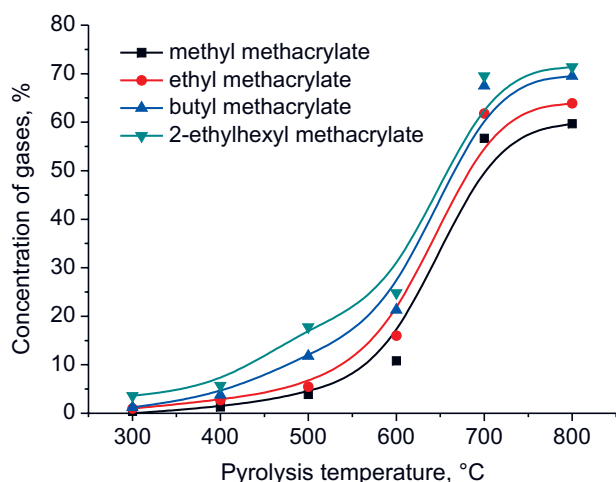


Figure 5. Influence of pyrolysis temperature on gases products yield during degradation of copolymers based on poly(alkyl methacrylates)
Rysunek 5. Wpływ temperatury pirolizy na tworzenie się produktów gazowych podczas degradacji termicznej kopolimerów na podstawie poli(metakrylanów alkilu)

tion, recombination etc. The process of diffusion of degradation products throughout the sample also plays an important role. The most important of these factors are the degradation conditions, which include temperature, heating rate, and the atmosphere in which the process occurs [7].

Figures 5-7 show the influence of pyrolysis temperature on major thermal breakdown products, such as gases (Fig. 5), monomers alkyl methacrylates (Fig. 6) and alcohols (Fig. 7) during the thermal degradation of copolymer based on poly(alkyl methacrylates) with different length of alkyl rest.

The major breakdown products from pyrolysis of copolymers based on poly(alkyl methacrylates) are gases containing carbon dioxide, carbon monoxide, methane and ethane, alkyl acrylates as accordingly monomers

and alcohols mixture containing methanol, ethanol and propanol (Tables 2-3). It was not observed the formation of typical breakdown products typically for poly(alkyl acrylates), such as alkenes, accordingly alcohols and acrylates. As regards the influence of temperature on the product distribution, high pyrolysis temperatures lead to increased amounts of typically products coming from thermal cracking reaction, such as carbon dioxide, carbon monoxide, methane, ethane, methanol, ethanol and propanol. The gases and alcohol yields increase with an increase of the pyrolysis temperature because the decarboxylation of the polymer chain accelerates at high temperatures [8].

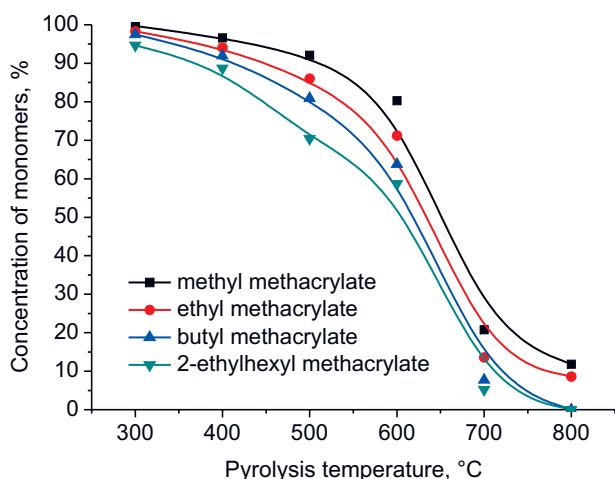


Figure 6. Influence of pyrolysis temperature on monomers yield during degradation of copolymers based on poly(alkyl methacrylates)

Rysunek 6. Wpływ temperatury pirolizy na tworzenie się monomerów podczas degradacji termicznej kopolimerów na podstawie poli(metakrylanów alkilu)

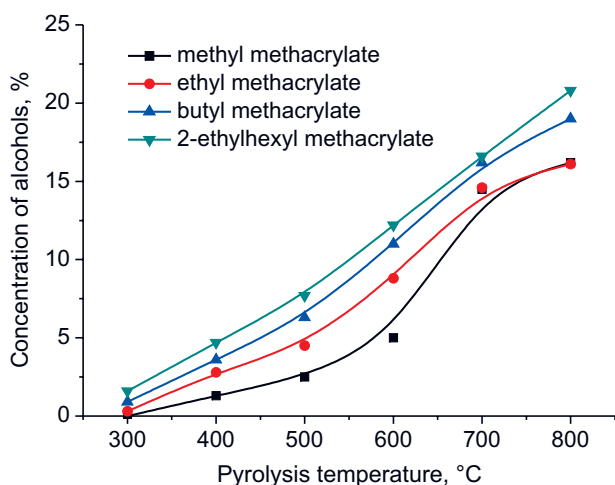


Figure 7. Influence of pyrolysis temperature on alcohols yield during degradation of copolymers based on poly(alkyl methacrylates)

Rysunek 7. Wpływ temperatury pirolizy na tworzenie się alkoholi podczas degradacji termicznej kopolimerów na podstawie poli(metakrylanów alkilu)

The evolution of the major breakdown product during the pyrolysis of copolymers based on poly(alkyl methacrylates), namely the accordingly monomers alkyl methacrylates is illustrated in Fig. 8.

The principal pyrolysis products of copolymers based on poly(alkyl methacrylates) are typical for poly(alkyl methacrylates) and 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 dependent upon the pyrolysis temperature. The concentration of monomers was measured at different

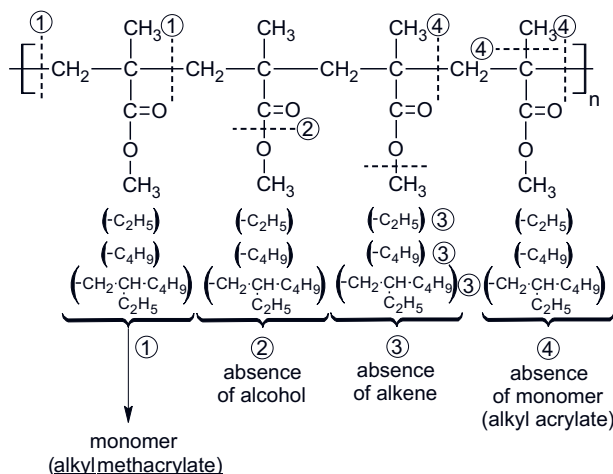


Figure 8. Thermal degradation mechanism of poly(alkyl methacrylates)

Rysunek 8. Mechanizm degradacji termicznej poli(metakrylanów alkilu)

pyrolysis temperatures between 300°C and 800°C. Figure 7, which is the result of the present investigations, clearly shows that this concentration corresponds directly with kind of degraded polymers and pyrolysis temperature. From the quantitative results, it is possible to observe the effect of monomer yields, depending on the number of carbon atom 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 alkyl side chain in the poly(alkyl methacrylates) the less monomers were formed during the pyrolysis. This mechanism of thermal degradation presented in Figure 8 supports the absence of alkenes, accordingly alcohols and monomers alkyl acrylates, what excludes the pyrolysis mechanismus ②, ③ and ④. During cracking reactions, especially at higher temperatures, are formed gases products and mixture of low molecular alcohols [9].

4. Conclusions

These present investigations give the all-round picture of pyrolysis of poly(alkyl methacrylates) in the wide range of high temperatures and suggest simple degradation mechanism providing a satisfactory explanation for the formation of major breakdown products, namely accordingly alkyl methacrylates, such as metyl methacrylate, ethyl methacrylate, butyl methacrylate and 2-ethylhexyl methacrylate. Poly(alkyl methacrylates) undergo thermal degradation at high temperatures includes main chain scission. The concurrent reactions by the investigated conditions do not give rise to the formation of accordingly alkenes, acrylates or alcohols. The increase of pyrolysis temperature leads to higher yields of products coming from main and side chains at cracking temperatures, such as carbon dioxide, carbon mono-

xide, methane, ethane or low molecular alcohols. Poly(alkyl methacrylates) produce during thermal degradation monomer methacrylates as the predominant breakdown product in all tested pyrolysis conditions.

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