

# Investigation on the thermal degradation of poly-*n*-alkyl acrylates and poly-*n*-alkyl methacrylates (C<sub>1</sub>–C<sub>12</sub>)

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## Abstract

The thermal degradation of a series of poly-*n*-alkyl acrylates, from methyl to dodecyl, and poly-*n*-alkyl methacrylates, from butyl to nonyl, has been studied in isothermal conditions at 400–650 °C using pyrolysis-gas chromatography/mass spectrometry. The type and composition of the pyrolysis products gave useful information about the mechanism of thermal degradation. It was shown that the main thermal degradation processes for poly-*n*-alkyl acrylates are random main-chain scission with the formation of monomer, dimer, saturated diester, trimer, corresponding acetate and methacrylate, and non-radical side-chain reaction through six-member ring transition state. The most abundant degradation products coming from the alkyl ester decomposition are the corresponding olefin, aldehyde, and alcohol. Poly-*n*-alkyl methacrylates yield monomer as the predominant degradation product in all investigated pyrolysis conditions. Unlike poly(methyl methacrylate) which gives quantitative yields of monomer, however, the poly-*n*-alkyl methacrylates with longer alkyl chain produce also significant amounts of olefin and methacrylic acid.

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## 1. Introduction

The investigation of vinyl polymers attracts increasing attention because these polymers are being widely used in modern technological processes. These materials have to meet stringent requirements, and this stimulates both improvement of synthetic procedures and material properties analyses including thermal behaviour and degradation mechanism. Thermal decomposition of vinyl polymers is relevant to deterioration of materials properties during high-temperature processing. The use

of pyrolysis-based analytical techniques and pyrolytic methods to recover chemical feedstock from polymer waste are also of interest.

In previous work we studied the thermal degradation of a series of poly-4-*n*-alkylstyrenes with long alkyl chain by pyrolysis-gas chromatography techniques [1].

The thermal behaviour of polyacrylates, polymethacrylates, and also acrylate–methacrylate copolymers has been the subject of some reports [2–7]. However, there has been no study of any series of polymers with systematically varied linear unbranched alkyl substituents, which are very important for the synthesis of industrial copolymers. For this purpose, the representative series of poly-*n*-alkyl acrylates (PAA) ranging from poly(methyl acrylate) (PAA-1) to poly(dodecyl acrylate) (PAA-12), and of poly-*n*-alkyl methacrylates (PMA)

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Table 1  
Molecular weight characteristics of PAA-*n*

	$M_w \times 10^{-3}$	$M_n \times 10^{-3}$	$M_w/M_n$
PAA-1	111	36	3.1
PAA-2	118	32	3.7
PAA-3	115	31	3.7
PAA-4	111	30	3.7
PAA-5	111	34	3.3
PAA-6	124	32	3.9
PAA-7	109	30	3.6
PAA-8	131	31	4.2
PAA-9	102	25	4.1
PAA-11	92	27	3.4
PAA-12	88	21	4.2

ranging from poly(butyl methacrylate) (PMA-4) to poly(nonyl methacrylate) (PMA-9), have been investigated by pyrolysis-gas chromatography/mass spectrometry.

## 2. Experimental

### 2.1. Materials

The polymerisation of *n*-alkyl acrylates and *n*-alkyl methacrylates was carried out on bulk samples in argon atmosphere in the presence of benzoyl peroxide (0.2 wt%) at 70 °C for 24 h. All monomers were commercially available from Reaxim (Russia) with the exception of *n*-heptyl and *n*-octyl methacrylates which were synthesized from methacrylic acid and the corresponding alcohols. The molecular weight characteristics of PAA-*n* and PMA-*n* are given in Tables 1 and 2, respectively. Size exclusion chromatography (SEC) analyses were carried out in THF using a KhCh-1039 liquid chromatograph (Russia) equipped with a 0.5 × 400 mm column, sorbent Ultrastayragel (10<sup>3</sup>, 10<sup>4</sup>, and 10<sup>5</sup> Å pore size) and home made UV (260 nm) detector [8]. The system was calibrated using a set of

Table 2  
Molecular weight characteristics of PMA-*n*

	$M_w \times 10^{-3}$	$M_n \times 10^{-3}$	$M_w/M_n$
PMA-4	141	37	3.8
PMA-5	247	52	4.7
PMA-6	134	32	4.2
PMA-7	119	27	4.4
PMA-8	151	39	3.9
PMA-9	108	32	3.4

narrow polystyrene standards with molar mass ranging from 400 to 1 × 10<sup>6</sup>.

### 2.2. Degradation procedure

The pyrolyses were carried out in a Chemical Data Systems Pyroprobe 2000 apparatus. The samples (0.4–0.5 mg) were placed in quartz tubes secured with plugs of quartz wool and inserted into the coil filament of the Pyroprobe. The coil probe was connected, through an interface maintained at 200 °C, into the injector of a Hewlett–Packard 6890 Plus gas chromatograph (GC) equipped with a flame ionisation detector (FID). The pyrolysis temperatures were set at 400, 450, 550 and 650 °C and the pyrolysis time was 10 s. The rate of temperature increase was about 60 °C/ms. A split ratio of 1:5 was maintained at the capillary injection port. As the separation column, a fused silica capillary column Supelco SPB-5, 30 m × 0.32 mm i.d., with a film thickness of 0.25 µm, was used. The oven was set at 30 °C for 2 min, then heated to 290 °C at a rate of 8 °C/min, holding the final temperature for 15 min. Data acquisition was accomplished with a Hewlett–Packard ChemStation. Due to the different response of the degradation products to FID, we have made a preliminary calibration using known amounts of reference compounds as external standards to avoid possible errors in the quantitative calculations. The tabulated yield values reported in Tables 3–6 are the averaged results of two or more runs.

Table 3  
Products (wt%) of PAA-*n* thermodegradation at 550 °C

	Light	Olefin	Alcohol	Aldehyde	Acetate	Monomer	Methacrylate	Diester	Dimer	Trimer
PAA-1	9.4	—	11.5	—	1.7	29.3	4.8	5.8	11.4	26.3
PAA-2		51.1 <sup>a</sup>	28.5		0.4	8.3	1.2	3.0	2.8	4.7
PAA-3		59.4 <sup>b</sup>	21.3	1.6	0.8	8.7	1.1	2.3	2.1	2.7
PAA-4	2.6	40.7	19.0	1.3	1.0	11.1	1.0	5.9	5.8	11.7
PAA-5	6.9	52.4	23.7	1.5	0.6	6.3	0.8	2.9	2.1	2.8
PAA-6	5.8	45.0	21.0	1.2	0.8	10.7	1.1	5.4	2.7	6.3
PAA-7	12.0	51.5	26.1	1.6	0.5	3.7	0.5	1.2	1.3	1.6
PAA-8	6.0	41.4	29.3	1.1	1.0	9.1	0.7	4.6	2.5	4.2
PAA-9	11.4	48.5	14.5	1.2	0.5	21.7	0.5	1.4	0.5	n.d.
PAA-11	10.6	55.5	22.6	1.0	1.1	4.7	0.8	2.6	1.1	n.d.
PAA-12	11.2	53.6	14.2	1.2	1.6	13.3	0.8	2.6	1.6	n.d.

<sup>a</sup> This value includes the light products, aldehyde, and olefin percentages.

<sup>b</sup> This value includes the light products, and olefin percentages.

Table 4

Products (wt%) of PAA-4, PAA-6, PAA-8, and PAA-12 thermodegradation at different temperatures (°C) of pyrolysis

	PAA-4			PAA-6			PAA-8			PAA-12		
	450 (°C)	550 (°C)	650 (°C)	450 (°C)	550 (°C)	650 (°C)	450 (°C)	550 (°C)	650 (°C)	450 (°C)	550 (°C)	650 (°C)
Light	0.2	2.6	4.9	1.2	5.8	26.4	0.9	6.1	12.7	1.7	11.1	19.5
Olefin	22.5	40.4	46.0	35.7	44.9	49.1	19.0	41.4	49.4	39.3	53.6	53.5
Alcohol	23.1	18.9	21.6	32.4	20.9	19.4	42.6	29.3	23.6	17.3	14.2	11.5
Aldehyde	<0.1	1.3	2.1	0.5	1.2	1.4	0.3	1.1	1.8	0.4	1.2	1.5
Acetate	0.6	1.0	1.0	0.6	0.8	0.1	0.8	1.0	0.8	2.1	1.6	1.0
Monomer	8.7	11.0	9.2	7.9	10.7	1.5	10.7	9.1	6.3	24.3	13.4	10.2
Methacrylate	0.4	1.0	1.1	1.1	1.1	0.7	0.3	0.6	0.4	0.5	0.8	0.4
Diester	8.9	5.8	3.6	7.7	5.4	0.6	9.5	4.6	2.1	7.8	2.6	1.4
Dimer	10.1	5.7	3.5	3.9	2.7	0.3	6.2	2.5	1.0	6.4	1.6	1.0
Trimer	24.0	11.6	6.7	8.8	6.2	0.5	9.7	4.3	1.8	n.d. <sup>a</sup>	n.d. <sup>a</sup>	n.d. <sup>a</sup>

<sup>a</sup> n.d. = Not detected.

Table 5

Products (wt%) of PMA-*n* thermodegradation at 550 °C

	Light	Olefin	Aldehyde	Alcohol	Methacrylic acid	Monomer
PMA-4	0.6	8.6	0.2	0.1	7.5	82.9
PMA-5	1.7	20.1	0.5	0.6	15.2	62.0
PMA-6	1.7	17.4	0.3	0.7	10.6	69.2
PMA-7	2.1	24.8	0.5	0.5	13.3	58.7
PMA-8	2.0	19.9	0.4	0.8	8.6	68.3
PMA-9	2.5	25.4	0.5	1.7	10.4	59.4

The identification of the degradation products was performed on a Hewlett–Packard 5985 B/5980 Series II gas chromatograph/mass spectrometer operating in an electron impact mode. The system was equipped with a capillary column identical to that used for pyrolysis-GC runs. Mass spectral data were obtained under the following conditions: ionising energy 70 eV; emission current 0.3 mA; ion source temperature 200 °C; transfer line temperature 280 °C; scanning rate 1.5 scans/s over the mass range  $m/z = 33$ –500.

### 3. Results and discussion

#### 3.1. Thermal degradation of poly-*n*-alkyl acrylates

In discussing the problems of thermal degradation of polymers, it should be emphasized that degradation

itself is a complex multistage process. It consists of a series of consecutive and simultaneous reactions of initiation, depolymerisation, scission of the side- and of the main chain of macromolecules, chain termination, recombination, etc. The process of diffusion of degradation products throughout the sample also plays a certain role. Each of the above reactions is characterized by its own kinetic parameters. Hence, each specific process has its own individual mechanism depending on a number of factors. The most important of these factors are the degradation conditions, which include temperature, heating rate, the atmosphere in which the process occurs, the aggregate state, the sample size, etc. Secondly, certain factors are the specific features of the chemical structure of sample: various defective units, end groups, impurities, etc. For these reasons the results reported by different authors are sometimes different.

Despite the close similarity in structure, it is well known that the PAA-*n* differ greatly in degradation behaviour from PMA-*n*. In Figs. 1 and 2 are reported the typical pyrograms of PAA-6 and PMA-6, respectively. Significant differences are observed between the pyrograms: the first is characterized by six major peaks, while the second one shows only an abundant peak due to the monomer.

The results of qualitative and quantitative investigations of PAA-*n* and PMA-*n* thermal degradation are summarized in Tables 3–6. In all tables we indicate as

Table 6

Products (wt%) of PMA-6 and PMA-9 thermodegradation at different temperatures (°C) of pyrolysis

	PMA-6				PMA-9		
	400 (°C)	450 (°C)	550 (°C)	650 (°C)	450 (°C)	550 (°C)	650 (°C)
Light	<0.1	0.4	1.7	5.6	0.6	2.5	7.0
Olefin	0.9	2.8	17.4	28.9	4.1	25.4	34.4
Aldehyde	0	0.1	0.3	0.7	0.1	0.5	0.9
Alcohol	0	0.6	0.7	0.5	3.1	1.7	2.5
Methacrylic acid	0.1	1.0	10.6	18.3	1.0	10.4	14.7
Monomer	98.9	95.1	69.2	45.9	91.0	59.4	40.4

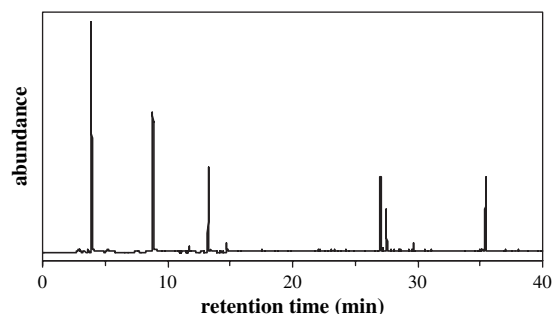


Fig. 1. Pyrogram of PAA-6 at 450 °C.

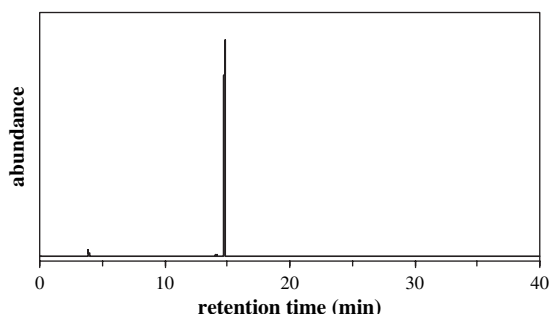


Fig. 2. Pyrogram of PMA-6 at 450 °C.

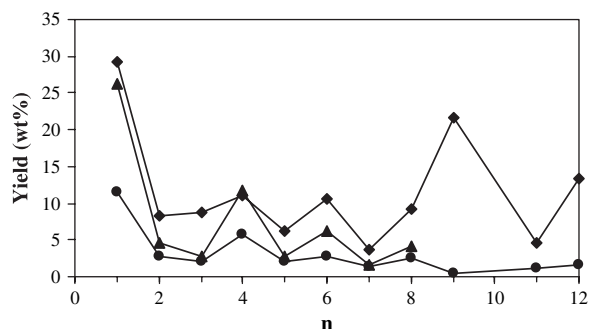
light products the obtained water, carbon dioxide, and various olefins with number of carbon atoms less than the side-chain carbon atom number of starting polymer.

The general mechanism of PAA-*n* thermal degradation includes random main-chain scissions and side-chain reactions. As results of random main-chain scission monomer, dimer, saturated diester, trimer, and corresponding acetate and methacrylate are formed (Scheme 1).

Because random main-chain scission takes place in condition of thermodynamic control, the quantitative yield depends on the stability of the formed radicals and compounds. Hence, trimer dominates dimer (Fig. 3), because the six-membered ring, whose formation is possible for trimer, is thermodynamically most stable in systems with carbon–carbon bonds [9].

The formation of energetically less favourable primary carbon radicals leads to acetate and methacrylate evolution. For this reason, we observe low amounts (wt%) of these products for all PAA-*n* investigated (Table 3).

As shown in Fig. 3, the yield of monomer in PAA-*n* series is stable and practically does not depend on the alkyl tail. A different behaviour is observed for PAA-1 and PAA-9. In the case of PAA-1 the high relative amounts of monomer, dimer, and trimer are due to the

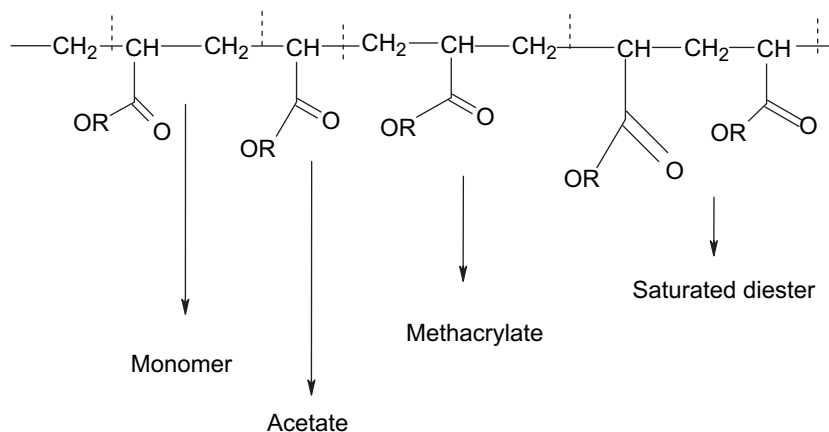
Fig. 3. Yield (wt%) of monomer (◆), dimer (●), and trimer (▲) in thermal degradation of PAA-*n* at 550 °C.

absence of long alkyl tail and, therefore, the impossibility of formation of other by-products. The behaviour of PAA-9 is unclear but repeated experiments gave similar results.

The occurrence of random main-chain scission in condition of thermodynamic control has been supported by the thermal degradation runs performed at different temperatures, from 450 to 650 °C.

The pyrolysis experiments carried out at 450 °C for 10 s are not complete. The amount of residue obtained ranges from 5 to 15%, independently from the length of the alkyl chain. Increasing the pyrolysis temperature practically does not change the qualitative distribution of the degradation products, but the yields (wt%) of the compounds coming from random main-chain scission decrease remarkably (Table 4). In Fig. 4 are reported the yields (wt%) of the heavy products, as sum of dimer, saturated diester, and trimer percentages, for different PAA-*n* samples at various temperatures. Moreover, the monomer formation decreases at 650 °C for all PAA-*n* studied.

Non-radical side-chain reactions are the second pathway occurring during PAA-*n* thermal degradations. The main products from these reactions are the corresponding olefin and alcohol (Table 3).



Scheme 1.

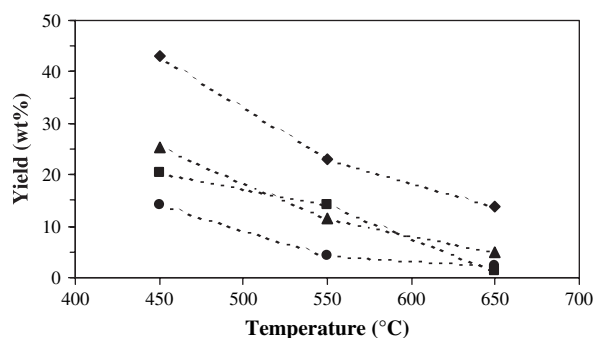


Fig. 4. Influence of temperature on heavy products yield (wt%) in PAA-4 (◆), PAA-6 (■), PAA-8 (▲), and PAA-12 (●) thermal degradation.

The formation of olefin takes place through six-membered ring transition state [2]. The elimination of the alkene leaves an acrylic acid unit in the polymer chain which cleaves the neighbouring ester fragment with the formation of alcohol and cyclic anhydride (Scheme 2). This mechanism supports the absence of acrylic acid among the decomposition products.

The six-membered transition state has partly aromatic character. It may undergo electrocyclic reactions such as 1,3-sigmatropic shift of proton or retro Diels–Alder reaction with the elimination of ethylene [8]. As shown in Scheme 3, 1,3-sigmatropic shift of proton from the alkyl chain to the carbonyl group leads to the formation of aldehyde.

Retro Diels–Alder reaction produces the elimination of ethylene leading to the formation of olefins with reduced number of carbons in relation to the alkyl tail of the starting polymer. This non-radical mechanism provides a satisfactory explanation of the formation of most products in PAA-*n* thermodegradation.

The relative percentages (wt%) of products forming from non-radical mechanism are practically the same for all PAA-*n* investigated (Table 3). Fig. 5 reports the yields (wt%) of the two main pyrolysis products, olefin and alcohol, deriving from non-radical side-chain reactions.

As regards the influence of temperature on the product distribution, high pyrolysis temperatures lead

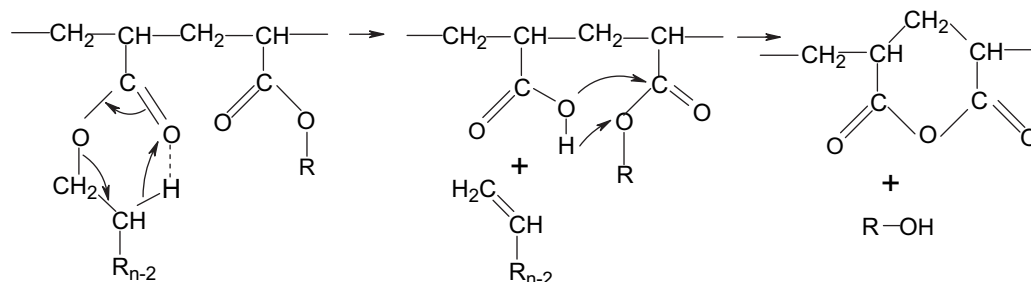
to increased amounts of products coming from non-radical mechanism such as olefin and aldehyde (Table 4). In contrast the alcohol yields decrease with an increase of the pyrolysis temperature because the decarboxylation of the intermediate free acid accelerates at high temperatures.

### 3.2. Thermal degradation of poly-*n*-alkyl methacrylates

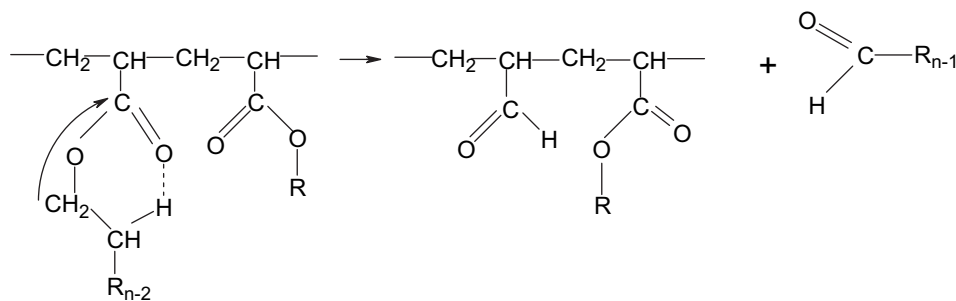
As shown in Figs. 1 and 2, despite the close similarity in structure, the degradation behaviours of PMA-*n* and PAA-*n* are not very similar. The main difference is that PMA-*n* give large yields of monomer. In our pyrolysis experiments performed at 550 °C for 10 s, the monomer account for 60–80 wt% of the total yield (Table 5). It is not surprising because the thermal degradation of poly(methyl methacrylate) is essentially a simple reverse of its polymerisation, leading to monomer in 100% yield [2]. After homolysis of the chain, the macroradicals depropagate with a very long zip length, so that chains of sufficiently low degree of polymerisation unzip completely. This mechanism leads to the absence of dimer, trimer and other by-products deriving from random main-chain scission among the PMA-*n* degradation products (Table 5).

From our quantitative results, it is possible to observe the odd–even effect of monomer yields, depending on the number of carbon atom in the alkyl side-chain. The amounts (wt%) of monomer for odd PMA-*n* are less than for even representatives of the series (Fig. 6).

In nature, effects of odd–even carbon number in alkyl chains of organic compounds exist in many areas of chemical applications. The difference of even and odd alkyl chains in the solid state is ascribed to the difference of packing in the crystal structure [10]. A different explanation, which is also applicable to solution properties, concerns the alternation of charge density in the alkyl chain [11]. This explanation may be applied to PMA-*n* thermal degradation results because the alternation of charge density in alkyl chain leads to different probability of six-membered transition state formation and, hence, to high or low yields of products



Scheme 2.



Scheme 3.

deriving from non-radical pathways. Finally, the odd–even effect on the probability of formation of a six-membered transition state may be ascribed to the alternating terminal methyl motions in the alkyl chains in relation to fixed motions near the carbonyl group in the *trans* conformation [12]. A choice between these explanations is impossible from our data.

The increase of pyrolysis temperature leads to significant decrease of monomer yield for all PMA-*n* studied because at higher temperatures the non-radical degradation processes become relevant (Table 6). For example, the PMA-6 monomer yield goes from nearly 100%, for pyrolysis carried out at 400 °C, to approximately 45%, for the experiment performed at 650 °C.

This behaviour resembles that of PAA-*n* series but some differences are concerned with the lower alcohol yields and the formation of significant amounts of methacrylic acid. The low alcohol content may be due to the stability of the cyclic anhydride of methacrylic acid. Firstly, the formation of cyclic anhydride of methacrylic acid is sterically hindered, in comparison with that of acrylic acid, by the presence of two methyl groups. Secondly, its temperature stability is low, in fact it begins to decompose at about 400 °C [12]. As a result, the alcohol formation pathway is hindered for PMA-*n*.

Another significant difference concerns the high content of methacrylic acid, whose yield increases with an increase of the pyrolysis temperature (Table 6). Ohtani et al. [13] ascribed the formation of methacrylic

acid by further thermal decomposition of free monomer at high pyrolysis temperatures. This proposed mechanism disagrees with our experimental data on PAA-*n* thermal degradation (Tables 3 and 4) which shows the absence of acrylic acid among the pyrolysis products, even for the degradations carried out at 650 °C. The formation of methacrylic acid may be explained by a non-radical side group ester decomposition leading to alkene and carboxylic acid [14].

#### 4. Conclusions

This work gives the full picture of thermal degradation of poly-*n*-alkyl acrylates and poly-*n*-alkyl methacrylates and suggests degradation mechanisms providing a satisfactory explanation for the formation of all destruction products.

The general mechanism of PAA-*n* thermal degradation includes random main-chain scission and side-chain reactions. These concurrent reactions give rise to the formation of monomer, dimer, trimer, alcohol, olefins, aldehyde, acetate, etc. The increase of pyrolysis temperature leads to higher yields of products coming from side-chain non-radical reactions, i.e. olefins, alcohol, and aldehyde.

Poly-*n*-alkyl methacrylates produce monomer as the predominant degradation product in all investigated pyrolysis conditions. The formation of methacrylic acid

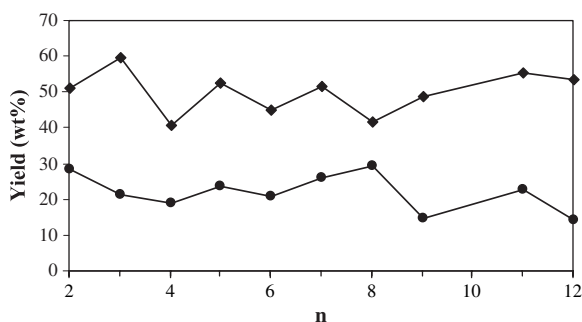


Fig. 5. Yield (wt%) of olefin (◆) and alcohol (●) in thermal degradation of PAA-*n* at 550 °C.

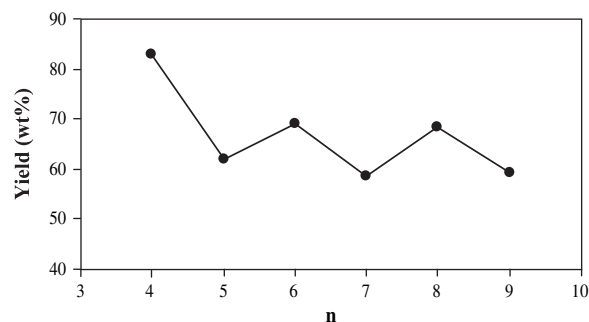


Fig. 6. Yield (wt%) of monomer in thermal degradation of PMA-*n* at 550 °C.

is also a characteristic process in PMA-*n* thermal degradation at high temperature.

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