

Thermal stability of poly(2-ethylhexyl acrylates) used as plasticizers for medical application

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Abstract This article discusses thermal analysis of different molecular weight poly(2-ethylhexyl acrylates) synthesized by radical polymerization of 2-ethylhexyl acrylate. The main aim of this work was to investigate the thermal properties and degradation process of synthesized acrylic homopolymers and forming of thermal degradation products during their pyrolysis. As investigated method pyrolysis combined with gas chromatography was used. Poly(2-ethylhexyl acrylates) are used as plasticizers for pressure-sensitive adhesives applied in medical area.

Keywords Thermal degradation · Plasticizer · Poly(2-ethylhexyl acrylate) · Gas chromatography · Pressure-sensitive adhesives (PSA)

Introduction

Almost every available polymeric materials have been used or can be used as a plasticizers material for surface coatings, film, sheeting, and pressure-sensitive adhesives (PSA). A plasticizer is a polymeric material incorporated into PSA to increase their peel adhesion, tack, and at the same time to improve their removability from skin, very important properties of medical products. New area

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applications for polymeric plasticizers based on 2-ethylhexyl acrylate (2-EHA) are technical products where the thermal resistance plays the major role.

The successful development of high performance acrylic polymers in form of copolymers and homopolymers used as PSA has been viewed as a classic example attesting to the importance of applying this kind of polymeric materials in a variety of application areas.

The investigation of acrylic polymers attracts increasing attention because these polymers are being widely used in modern technological processes. Poly(2-ethylhexyl acrylates) with different molecular weights are very important specialty products in the modern polymer chemistry. They are used in polymer technology as tackifiers or plasticizers for modification of PSA, especially PSA based on acrylics for medical application. Poly(2-ethylhexyl acrylates) are widely used in many areas of life for manufacturing of mounting tapes, splicing tapes, protective films, sign and marking films, and as components of pharmaceutical composition for biomedical electrodes, self-adhesive hydrogels, or kit for treating obesity and reducing absorption of fats by the mammals [1, 2]. Thermal decomposition of acrylic polymers is relevant and significant to deterioration of materials properties during high temperature processing, especially by extremely applications. The use of pyrolysis-based analytical techniques and pyrolytic methods to recover chemical feedstock from polymer waste are also of interest. The thermal behavior of acrylics, especially of acrylic copolymers used as self-adhesives, has been the subject of some reports [3–14].

Experimental

Synthesis of poly(2-ethylhexyl acrylates)

Poly(2-ethylhexyl acrylates) with different molecular weights were synthesized in ethyl acetate (boiling point 77 °C) using 2-EHA in the presence of radical starter AIBN in concentration between 0.1 % and 0.5 wt%. The polymerization was conducted by the use of following conditions:

- addition of monomer 2-EHA blended with AIBN in ethyl acetate before polymerization: 60 % weight,
- addition time of the rest of the mixture 2-EHA with AIBN: 1 h,
- post-reaction time: 4 h.

Viscosity and molecular weight of synthesized poly(2-ethylhexyl acrylates)

Viscosity of solvent-borne poly(2-ethylhexyl acrylates) was determined using a viscosimeter Rheomat RM (Rheometric Scientific) with nr 3 spindle in 23 °C. Molecular weight was determined with the use of liquid chromatograph LaChrom: RI Detector Li-7490 and LaChrom UV Detector L-7400 Merck Hitachi supplied with PLgel 10⁶ Hewlett-Packard column.

Table 1 Molecular weights and poly dispersities of acrylic polymers synthesized from 2-EHA

Concentration		Viscosity (Pa s)	\overline{M}_w	\overline{M}_n	$P_d = \overline{M}_w/\overline{M}_n$
2-EHA (wt%)	AIBN (wt%)				
99.9	0.1	16.8	645,000	207,000	3.12
99.8	0.2	11.9	571,000	155,000	3.68
99.7	0.3	8.7	492,000	122,000	4.03
99.6	0.4	5.4	423,000	87,000	4.86
99.5	0.5	3.1	312,000	55,000	

Thermal degradation process

Investigations of the thermal degradation of poly(2-ethylhexyl acrylates) were performed using a pyrolysis gas chromatography with the use of Intersmat IGC 131 chromatograph with capillary column (QC2/BP1) 25 m × 0.25 mm (100 % dimethyl polysiloxane). Helium (80 kPa) was used as carrier gas. Pyrolysis conditions: detector FID—250 °C, feeder temperature—250 °C, oven temperature program—from 50 to 230 °C with increment 10 °C/min (32 min), sample volume—0.3 µl. The products of the pyrolysis were swept into chromatograph column with nitrogen. The composition of the polymeric formula was determined by comparison of chromatogram of the sample with the chromatograms of known monomers and pyrolyzates of known polymers. The analysis of gaseous products was conducted using a isochoric manometer coupled with infrared spectroscopy.

Results and discussion

Characteristics of poly(2-ethylhexyl acrylate) homopolymers

The polymers synthesized based on 2-EHA with 60 wt% polymer content were characterized with following properties, such as viscosity, weight average molecular weight, number average molecular weight, and polydispersity (Table 1).

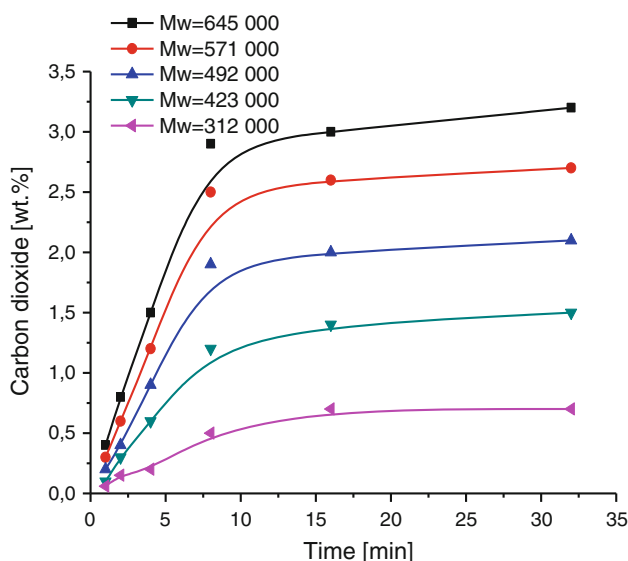
Influence of molecular weight of synthesized poly(2-ethylhexyl acrylates) on gaseous products concentration

The main gaseous products obtained after thermal degradation of poly(2-ethylhexyl acrylate) synthesized with molecular weight M_w 645,000 and presented in Table 2 are carbon dioxide between 0.4 and 3.2 wt% and non-identified products in the concentration between 0.1 and 1.1 wt%. The amounts of carbon dioxide, formed during pyrolysis of all synthesized poly(2-ethylhexyl acrylates) with different molecular weights, are illustrated in Fig. 1.

The amounts of carbon dioxide depend on the molecular weight of synthesized polymers based on 2-EHA. With increasing of the molecular weight of synthesized poly(2-ethylhexyl acrylates) the concentration of carbon dioxide formed increases.

Table 2 Forming of gaseous and liquids products by thermal degradation of poly(2-ethylhexyl acrylate) with molecular weight M_w 645,000 as a function of pyrolysis time

Products of pyrolysis	Products of thermal degradation of poly(2-ethylhexyl acrylate) (wt%)					
	1 min	2 min	4 min	8 min	16 min	32 min
Total volatile components						
Residue (soluble)	84.0	78.1	69.4	57.2	41.1	15.8
Chain fragments						
2-EHA	12.8	15.6	17.9	19.3	25.0	41.9
2-EHMA	2.7	4.4	6.1	7.0	10.0	14.1
Liquids						
2-ethyl-hexanol-1	0.0	0.9	3.6	9.1	14.3	17.3
2-ethyl-hexene-1	0.0	0.0	1.2	4.1	5.7	6.6
Non-condensable gases						
Carbon dioxide	0.4	0.8	1.5	2.9	3.0	3.2
	0.1	0.2	0.3	0.4	0.9	1.1

**Fig. 1** Forming of carbon dioxide during pyrolysis of poly(2-ethylhexyl acrylates)

The amounts shown in Table 2 are measured after 32 min thermal degradation time from 0.6 wt% for homopolymer with the lowest molecular weight M_w of 312,000–3.2 wt% for poly(2-ethylhexyl acrylate) with the highest molecular weight M_w of 645,000 (Fig. 1). Perhaps, higher degradation rate can be attributed to higher mobility of higher molecular weight chains allowing faster rearrangement of the pedant molecular groups during decarboxylation, observed as carbon dioxide formation (Fig. 2).

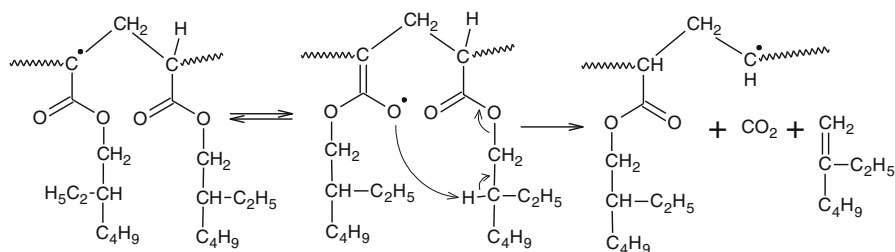


Fig. 2 Reaction of thermal degradation of poly(2-ethylhexyl acrylates) with carbon dioxide and olefin forming

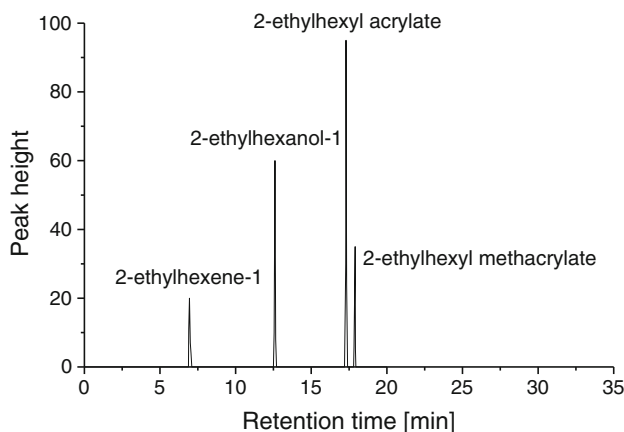


Fig. 3 Chromatogram of liquid products of degradation of investigated poly(2-ethylhexyl acrylates)

Kind of liquid products

The liquid products of poly(2-ethylhexyl acrylate) degradation were analyzed using gas chromatography and illustrated in Fig. 3, which presents liquid products of thermal degradation of poly(2-ethylhexyl acrylates) such as olefin 2-ethylhexene-1, alcohol 2-ethylhexanol-1, and monomers: 2-EHA and corresponding 2-ethylhexyl methacrylate (2-EHMA), which are connected with decomposition of the main chain of homopolymer. Results of this investigation in dependence of time of the pyrolysis are presented in Table 2.

Concentration of the 2-ethylhexene-1 forming seems to vary as the number of β -hydrogen atoms in the alkyl group of monomer. In each of the polymers molar ratio of olefin to carbon dioxide is of the order of unity over a substantial part of the reaction. Contents of the degradation products of poly(2-ethylhexyl acrylate) with the highest molecular weight of 645,000 are presented in Table 2. In each of the synthesized homopolymers based on poly(2-ethylhexyl acrylates) a formation of 2-EHA and 2-EHMA was confirmed (Fig. 3) as a result of decomposition of main chain of acrylic polymer synthesized during radically polymerization. Retention time values of 2-ethylhexene-1, 2-ethylhexanol-1, 2-EHA, and 2-EHMA are

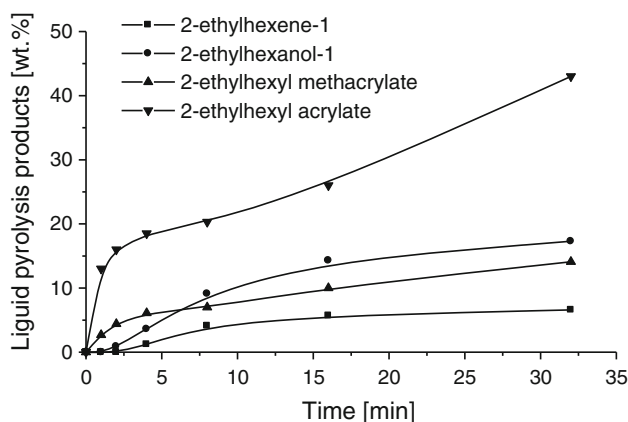
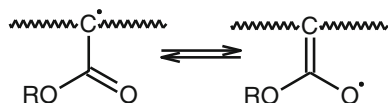


Fig. 4 Forming of liquid products by thermal degradation of poly(2-ethylhexyl acrylate) with molecular weight M_w of 645,000

Fig. 5 Radical responsible for thermal decomposition of poly(alkyl acrylates)



presented in Fig. 3, and their concentrations for poly(2-ethylhexyl acrylates) are characterized by molecular weight M_w of 645,000 in Fig. 4.

It can be suggested that because of relatively low volatility of monomers the 2-EHA and 2-EHMA is formed; the mechanism of thermal reactions that appear in a case of 2-EHA and similar polymers, a free-radical course is not involved. In fact small molecules of ester do not normally undergo decomposition under 400 °C. In polymer environment and especially when radical is stabilized by the resonance or the inductive effects, there is an overwhelming proof for proceeding of free-radical mechanism under 300 °C [4]. Indeed, in temperatures above 280 °C decomposition mechanism without involving free radicals is rare. Initial step during acrylates degradation is probably decomposition in some unspecified point of the polymer molecule [5]. It will be proposed that initially formed free radicals would remove tertiary hydrogen atoms from the polymer backbone giving relatively stable radical (Fig. 5) and all the major decomposition reactions in poly(alkyl acrylate) are initiated by this radical.

The evidence confirming this theory for other poly(alkyl acrylates) are thermograms and comparability of their characteristic products of decomposition. A difficulty was to explain how these products could be formed in one step unless all of reactions would have one precursor. During thermal degradation of poly(2-ethylhexyl acrylates), carbon dioxide and olefin are formed in molar ratio close to unity, at least in early stages of the reaction. Therefore, it seems that reaction proceeds according to type I (Fig. 2) or type II (Fig. 6).

The amounts of volatile condensable and non-condensable gases were always small (less than 4.2 wt%). Probably carbon dioxide was the main non-condensable

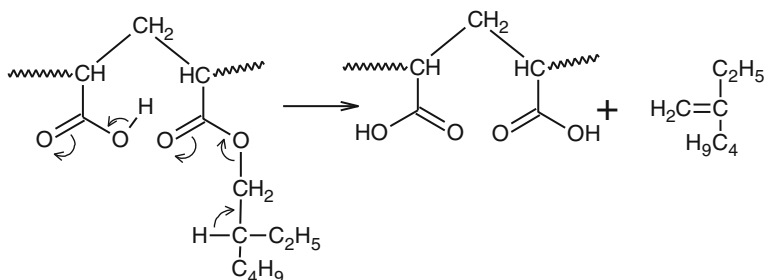


Fig. 6 Reaction of thermal degradation of poly(2-ethylhexyl acrylates) with olefin forming

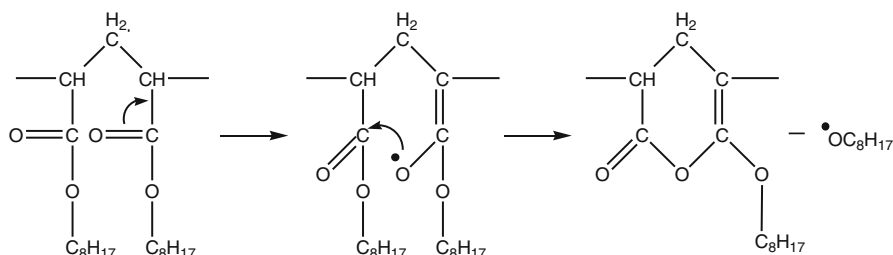


Fig. 7 Reaction of thermal degradation of PSA with alcohol and double bonds forming

product. There is no proof for autocatalytic production of olefin; therefore, competition of reaction type I and reaction type II, proposed in order to explain autocatalytic decomposition of 2-EHA is acknowledged as insignificant. However, reaction type I is shown as catalyzed by the radical on a neighboring monomer unit, which does not exclude why every available radical could not be an initiator. The reaction type I is in close relation between forming an olefin and number of β -hydrogen atoms in the alkyl group. In that case ester 2-ethylhexyl is connected with monomers of acrylate and methacrylate, which have relatively low volatility in poly(2-ethylhexyl acrylates). The fraction forming from this part of chain is usually yellow color and the intensity of the color increases with the time of degradation.

Conclusions

The investigations on poly(2-ethylhexyl acrylates) characterized by different molecular weights were successfully conducted. The results showed that main gaseous product of pyrolysis was carbon dioxide and 2-ethylhexene-1. 2-Ethylhexanol-1, 2-EHA and 2-EHMA were the main liquid products of pyrolysis during thermal degradation of synthesized poly(2-ethylhexyl acrylates). The forming mechanism of all previously mentioned compounds could be explained with characteristic properties of typical poly(2-ethylhexyl acrylates), which easily undergo pyrolytic decomposition to carbon dioxide and derivatives of 2-ethylhexyl corresponding to the main component of the ester of acrylic PSA.

The residual homopolymers synthesized from poly(2-ethylhexyl acrylates) become more intensely colored with progression of degradation. The color is probably a result of mainly coupled double carbon–carbon bonds but it is also possible due to carbonyl groups. Double carbon–carbon bonds formed in polymer during reaction are shown in Fig. 7 or as a result electron transfer reaction.

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