

# Pyrolysis of poly(2-propylheptyl acrylate)

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Received: 13 October 2009 / Accepted: 3 December 2009 / Published online: 7 January 2010  
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**Abstract** The thermal destruction processes of poly(2-propylheptyl acrylate) take place at the range of temperature 250–950 °C was investigated using pyrolysis–gas chromatography. Knowledge of the types and amounts of pyrolysis products will provide important information about the thermal degradation of homopolymer poly(2-propylheptyl acrylate) and the mechanisms involved. Unsaturated monomers 2-propylheptyl acrylate and 2-propylheptyl methacrylate, according to by-product alkyl alcohol 2-propylheptyl alcohol, alkene 2-propylheptene-1, carbon dioxide, carbon monoxide, methane, and ethane were formed during thermal degradation of poly(2-propylheptyl acrylate).

**Keywords** Acrylic homopolymer · Poly(2-propylheptyl acrylate) · Pyrolysis · Solvent-based polymerization · Thermal decomposition · Thermal destruction

## Introduction

The chemical nature of the thermal decomposition of polymers varies widely from one material to another. At its simplest it may consist of complete breakdown to a single, and readily identifiable product which is often monomer. On the other hand, a complex mixture of products may be obtained together with a relatively stable intractable residue. From the point of view of identification, there are three

types of products of thermal degradation [1, 2]. First, substances of the molecular dimensions of monomer or less, of which a detailed analysis can usually be made. Second, substances are often produced which are volatile at the degradation temperatures, but involatile at ordinary temperatures. These are usually polymer chain fragments which are larger than monomer. Although, they may be referred to as dimeric, trimeric, etc., their precise chemical structures have usually not been determined. Finally, the involatile residue which often remains is frequently insoluble although knowledge of the mechanism of the degradation reaction combined with spectral data can often give some information about its structure. The relative amounts of these three kinds of products can vary with the temperature of degradation, although no a great deal of information of this kind is available. However, the temperature ranges, in which the experiments have been carried out, are quoted in the table since they give some idea of the relative stability of the polymers [3–8].

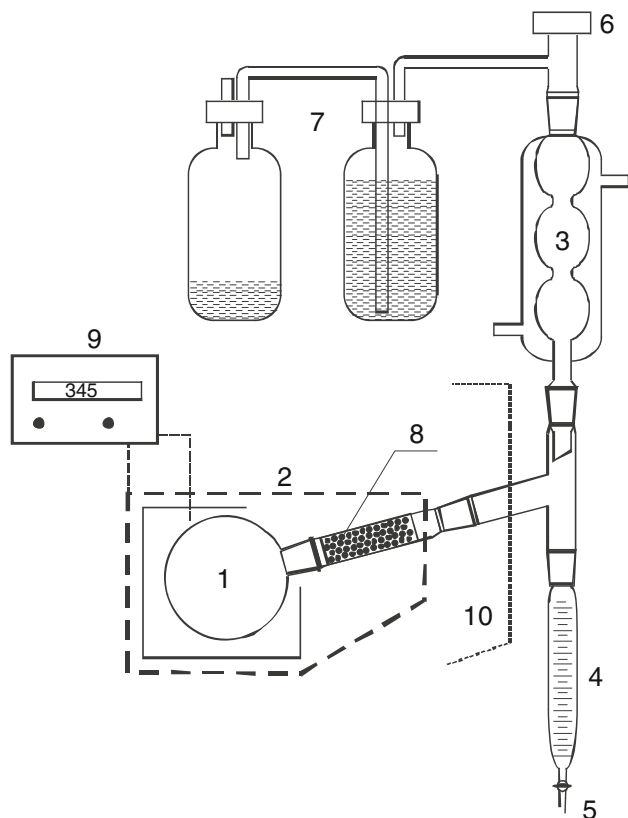
Most of the data are concerned with the volatile small molecular products of degradation. Information about larger chain fragments and involatile residues is given, where it is available and relevant.

The successful development of high-performance polymers containing polymer plasticizers with low glass transition temperature ( $T_g$ ), such as poly(2-propylheptyl acrylate), has been viewed as a classic example attesting to the importance of applying novel materials in a variety of application areas [9]. Polymers employed as PSAs have to fulfill partially contradictory requirements; they need to adhere to substrates, to display high shear strength, and peel adhesion, and not leave any residue on the substrate upon debonding. In order to meet all these requirements, a compromise is needed. When using PSAs, there appears another difference with wet adhesives, namely the adhesive does not

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**Table 1** Molecular mass of synthesized homopolymer poly(2-propylheptyl acrylate)

| $\bar{M}_w$ Dalton | $\bar{M}_n$ Dalton | $P_d = \frac{\bar{M}_w}{\bar{M}_n}$ |
|--------------------|--------------------|-------------------------------------|
| 645 700            | 145 600            | 4.43                                |

**Fig. 1** Pyrolysis setup: 1—quartz flask, 2—electric furnace, 3—condenser, 4—liquid products collector, 5—blowdown valve, 6—septas, 7—hydraulic valve, 8—quartz balls, 9—temperature controller, 10—thermal insulation

change its physical state because film forming is inherent to PSAs. Novel acrylic PSAs for PVC application as sign and marking films contain polymeric plasticizers. The best results have been achieved using poly(2-propylheptyl acrylate).

The investigation of polymers containing polymer plasticizers attracts increasing attention because these kinds of polymers are being widely used in modern technological processes and coatings, such as for manufacturing of decorative films, and sign and marking films. These materials have to meet stringent requirements, and this stimulates both improvement of synthetic procedures and material properties analyses including thermal behavior and degradation mechanism. Thermal decomposition of polymers including polymer plasticizers is relevant and

significant 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 [10, 11].

## Experimental

### Materials

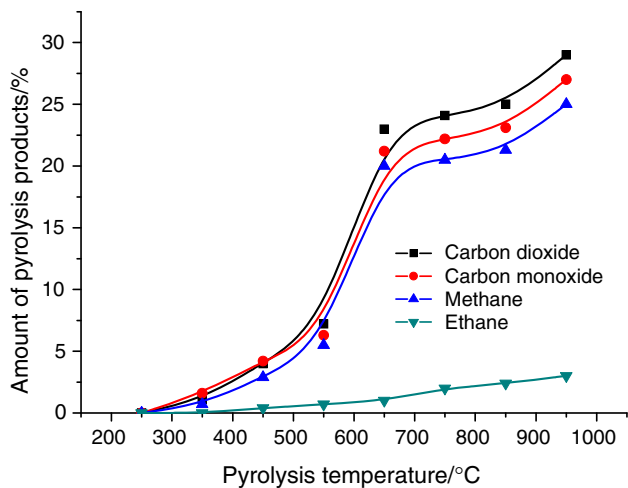
The polymerization of 2-propylheptyl acrylate (BASF, Germany) was conducted on bulk samples in an argon atmosphere in the presence of 2,2'-azo-bis-diisobutyronitrile (AIBN; ChemCycle, Germany) as a thermal initiator to start radical polymerization in concentration of 0.1 wt% according to polymerized monomer at 80 °C during 6 h. The synthesized homopolymer was characterized according to mass average molecular mass ( $\bar{M}_w$ ), number average molecular mass ( $\bar{M}_n$ ), and polydispersity ( $P_d$ ; Table 1). The molecular mass studies were performed in tetrahydrofuran with a liquid chromatograph LaChrom system: RI Detector L-7490 and LaChrom UV Detector L-7400 from Merck-Hitachi, equipped with a PLgel 106L column from Hewlett-Packard.

### Degradation process

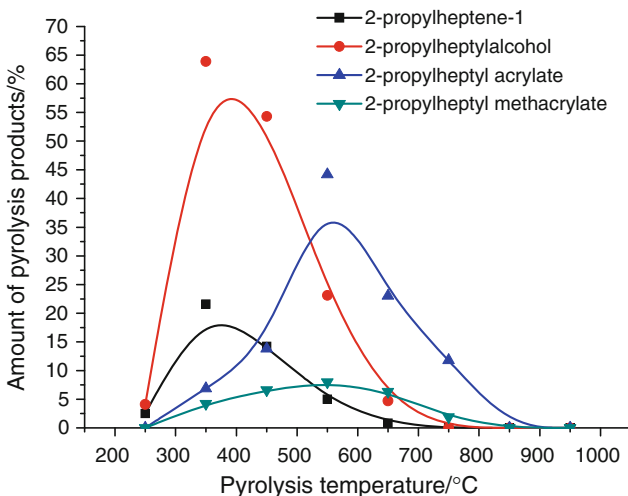
The pyrolysis processes were carried out in the system showed that on Fig. 1. The sample of 5 g adhesive was placed in a quartz flask (1) and it was heating in electrical furnace (2) to the required temperature. The quartz flask was connected with the condenser (3) where the evolved

**Table 2** Composition of breakdown products of poly(2-propylheptyl acrylate)

| Pyrolysis products          | Pyrolysis temperature/°C             |      |      |      |      |      |      |      |
|-----------------------------|--------------------------------------|------|------|------|------|------|------|------|
|                             | 250                                  | 350  | 450  | 550  | 650  | 750  | 850  | 950  |
|                             | Mass percent of original homopolymer |      |      |      |      |      |      |      |
| Carbon dioxide              | –                                    | 1.1  | 4.0  | 7.2  | 20.3 | 23.2 | 23.0 | 27.0 |
| Carbon monoxide             | –                                    | 1.6  | 4.2  | 6.3  | 19.1 | 21.4 | 21.6 | 25.4 |
| Methane                     | –                                    | 0.7  | 2.9  | 5.5  | 18.5 | 20.5 | 20.5 | 22.8 |
| Ethane                      | –                                    |      | 0.4  | 0.7  | 1.0  | 2.0  | 2.4  | 3.0  |
| 2-propylheptene-1           | 2.5                                  | 20.1 | 12.2 | 5.0  | 0.8  | –    | –    | –    |
| 2-propylheptanol-1          | 4.1                                  | 58.1 | 49.2 | 20.2 | 4.7  | –    | –    | –    |
| 2-propylheptyl acrylate     | –                                    | 6.6  | 12.7 | 37.8 | 20.5 | 10.9 | –    | –    |
| 2-propylheptyl methacrylate | –                                    | 3.9  | 6.4  | 7.7  | 6.3  | 1.9  | –    | –    |
| Other gas by-products       | –                                    | –    | –    | –    | –    | 10.6 | 21.1 | 10.4 |
| Carbon residue              | –                                    | 6.9  | 5.9  | 6.1  | 5.7  | 5.8  | 5.5  | 5.6  |



**Fig. 2** Amount of gas breakdown products of poly(2-propylheptyl acrylate) as a function of pyrolysis temperature

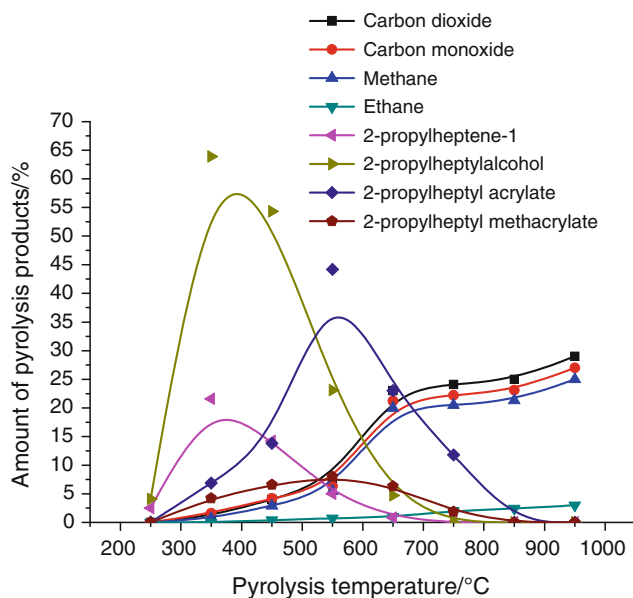


**Fig. 3** Amount of characteristic liquid breakdown products of poly(2-propylheptyl acrylate) as a function of pyrolysis temperature

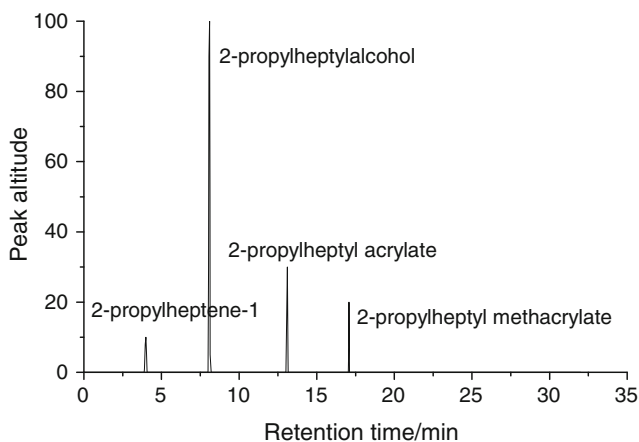
liquid products were condensed and collected in a liquid products collector (4). The liquid products collector possessed blown down valve (5) that enabled the liquid sample drawing. The condenser outlet was closed by hydraulic valve (6) that enabled the gaseous products collecting. On top of the condenser there was a septa (7) that enabled the pyrolysis gaseous sample drawing.

**Analytical methods**

The quantitative and qualitative analyses were conducted using gas chromatography method. The determination of liquid products were conducted with an external standard method and following analytical conditions: gas



**Fig. 4** Amount of all breakdown products of poly(2-propylheptyl acrylate) as a function of pyrolysis temperature

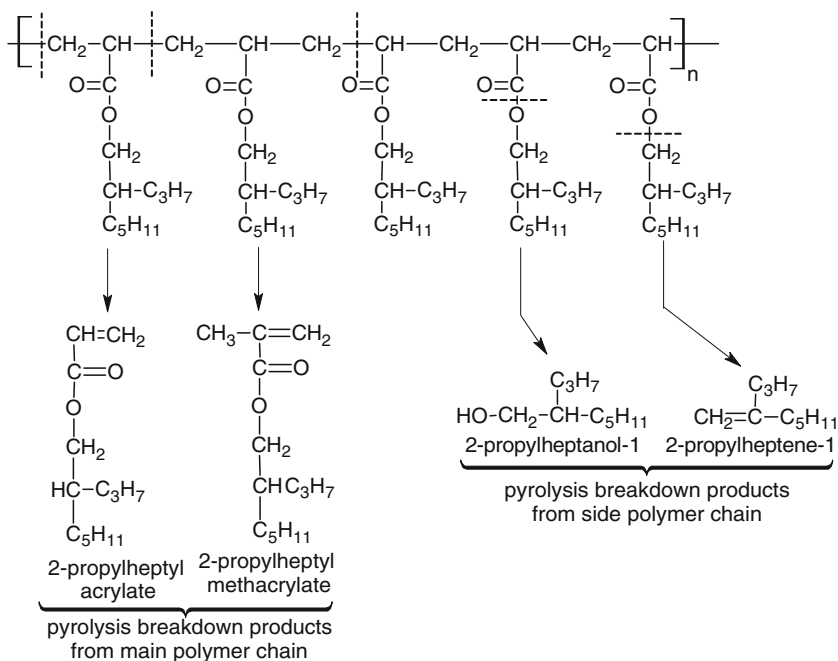


**Fig. 5** GC of the liquids degradation products of evaluated acrylic polymer

chromatograph ThermoScientific GC8000<sup>TOP</sup>, capillary column—RESTEK RTX-5 30 m × 0.53 mm, 1.5 μm film, carrier gas—He 5 cm<sup>3</sup> min<sup>-1</sup>, 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<sup>-1</sup>.

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 cm<sup>3</sup> min<sup>-1</sup>, detector temperature (TCD)—200 °C, injector temperature—100 °C, oven temperature program—45 °C (10 min) to 250 °C at 10 °C min<sup>-1</sup>.

**Fig. 6** Mechanism of thermal degradation of poli(2-propylheptyl acrylate)



## Results and discussion

The breakdown products of poly(2-propylheptyl acrylate) between 250 and 950 °C are summarized in Tables 1 and 2, which also shows a very sharp change in the concentration of the breakdown products, but now in a different temperature range.

The major gaseous products (Fig. 2) were carbon dioxide, carbon monoxide, methane, and ethane. The amounts of carbon dioxide (about 29 wt%), carbon monoxide (about 27 wt%), methane (about 25 wt%), and ethane (about 3 wt%) at higher temperatures in the range of 650–950 °C increases very sharply.

The major gaseous products carbon dioxide, carbon monoxide, methane, and ethane corresponding to the ester group in the polymer. The amounts of gases volatile at pyrolysis temperature to about 350 °C were always very small, and were only analyzed at an advanced extent of thermal degradation. Other gas by-products are unidentified decomposition products. At lower temperatures, the polymer degrades nearly completely to the by-products, such as olefin 2-propylheptene-1, alcohol 2-propylheptanol-1, monomers 2-propylheptyl acrylate, and 2-propylheptyl methacrylate (Fig. 3), and gases appear only in small quantities. With rising temperatures, the monomers content decreases slowly, while the gas content simultaneously increases (Table 2). The liquid products were subjected to quantitative GC analysis. A chromatogram typical of all four liquid breakdown products shows clear that the 2-propylheptanol-1 is the major product with smaller amounts of

2-propylheptene-1 and the monomer 2-propylheptyl acrylate and the responding 2-propylheptyl methacrylate. It was confirmed that the corresponding methacrylate is a genuine degradation product, and was not present in the monomer used to prepare the polymer.

The concentrations of olefin 2-propylheptene-1 and of alcohol 2-propylheptanol-1 show maximums at temperature of 350 °C for 63.9 wt% 2-propylheptanol-1 and for 21.6 wt% 2-propylheptene-1 (Table 2). Between 550 and 750 °C, however, the monomer 2-propylheptyl acrylate concentration drops sharply from about 44.2 wt% to about 11.9 wt%, and monomer 2-propylheptyl methacrylate from about 8.0 wt% to about 1.9 wt%. At the same time, the amount of gases increases very sharply. In order to emphasize this effect, in Fig. 4, the amounts of the all identified pyrolysis by-products from Table 2 are plotted as a function of pyrolysis temperature. Here again, the breakdown products above 900 °C are composed only of gases.

The liquid products from the investigated polymer formed from 2-propylheptyl acrylate were analyzed by GC (Fig. 5).

The following peaks are characterized for 2-propylheptene-1, 2-propylheptanol-1, 2-propylheptyl acrylate, and 2-propylheptyl methacrylate. The evolution of the mentioned breakdown products is illustrated in Fig. 6.

The principal degradation of poly(2-propylheptyl acrylate) is illustrated in Fig. 6. The characteristics of the production of olefin 2-propylheptene-1 and alcohol 2-propylheptanol-1 are quite different, so that one may

reasonably presume that they are formed in quite distinct ester decomposition processes. Olefin and carbon dioxide are evolved from the polymer in a molar ratio close to unity, at least in the early stages of the decomposition reaction between ester groups [7]. Carbon dioxide production exceeds that of olefin all longer reaction time or in higher temperatures in degradation systems involving acrylate units. Production of alcohol, in this case of 2-propylheptanol-1, was explained in [8]. The mechanisms proposed for alcohol production are all initiated by the same polymer degradation (Fig. 6), as are the other component parts of the overall reaction, and since no other part of the reaction is autocatalytic, there is no obvious direct chemical route by which the products of the alcohol elimination reaction might facilitate further production of alcohol.

## Conclusions

This study examined the thermal degradation of acrylic homopolymer PSAs based on 2-propylheptyl acrylate at temperatures between 250 and 950 °C. The results showed that carbon dioxide, carbon monoxide, methane, and ethane were the major gaseous pyrolysis products, and the major thermal degradation liquid products were 2-propylheptene-1, 2-propylheptanol-1, 2-propylheptyl acrylate, and 2-propylheptyl methacrylate. The alcohol 2-propylheptanol-1 and olefin 2-propylheptene-1 corresponding to the alkyl group, although at pyrolysis temperatures between 350 and 450 °C, in acrylic polymer. The chain fragment fractions in form of monomer 2-propylheptyl acrylate and the corresponding of methacrylate are formed at 550 °C in biggest

concentration. The mechanism of formation of these founded major components can be explained by the characteristic properties of acrylic polymers.

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