Polymer Degradation and Stability 98 (2013) 502–507

Contents lists available at SciVerse ScienceDirect

Polymer Degradation and Stability

journal homepage: www.elsevier.com/locate/polydegstab

Thermal decomposition of poly(vinyl chloride) in organic solvents under high pressure

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ARTICLE INFO

Article history:
Received 19 September 2012
Accepted 10 December 2012
Available online 19 December 2012

Keywords:
PVC
Thermal decomposition
Organic chlorine compounds
High pressure
1,4-dichlorobutane

ABSTRACT

In order to study chlorination of the plastics derived liquid products by secondary reaction of hydrogen chloride, thermal decomposition of poly(vinyl chloride) (PVC) was carried out in decalin or tetralin at 300–460 °C for 0–90 min under 4.0 MPa of initial nitrogen pressure. Dechlorination of PVC was completed in 30 min at 300 °C, and further slight degradation of the dechlorinated PVC was observed in both solvents. Conversion of PVC to its liquid product proceeded with time at 400 °C, and much more liquid product was produced in tetralin than in decalin. In the liquid product, 1,4-dichlorobutane was observed as the dominant organic chlorine product at 300 °C, and its yield increased with the reaction time in both solvents. We detected 1,3-dichlorobutane, 1-chlorobutane, 2-chlorobutane, and chlorinated solvents as minor organic chlorine products. These results suggest that 1,4-dichlorobutane is a unique product of the secondary reaction between gaseous hydrogen chloride and the polyene chain derived from the dechlorination of PVC. In decalin, the yield of 1,4-dichlorobutane decreased with temperature, and the maximum yield of chlorodecalin was observed at 400 °C. Conversely, yields of all organic chlorine compounds decreased with the reaction time in tetralin, and this hydrogen donorable solvent effectively prevented the production of organic chlorine compounds.

1. Introduction

Reuse of waste plastics as an energy source or as raw chemical materials is very important not only to decrease environmental impacts but also to save limited natural organic resources. Because of the rapid increase in crude oil prices, waste plastics are now recognized as an important domestic energy resource. A few decades have passed since waste plastic was identified as an important environmental problem; yet more than 20% of waste plastics discarded in Japan are incinerated or deposited in landfills without energy recovery, and more than 50% are used as energy sources at low efficiency [1]. The chlorine contained in poly(vinyl chloride) (PVC) is one of the main reasons why waste plastics are difficult to use as energy resources.

The thermal decomposition of plastics comprising polyethylene (PE), polypropylene (PP), and polystyrene (PS) is effective when a solid acid catalyst is used [2]. However, the liquid fuel derived from post-consumer plastic waste containing PVC is contaminated by numerous organic chlorine compounds [3]. A number of characteristic organic chlorine compounds have been detected following the pyrolysis of PVC alone or in mixed plastics [4–7]. Thermal decomposition of PVC is carried out via three steps: dehydrochlorination [8] by a zipper reaction [9] at 200–320 °C, production of hydrogen chloride and benzene at 250–375 °C, and condensation of the dehydrochlorinated PVC to polycyclic aromatic compounds at 375–520 °C [10] [11],. To reduce the chlorine content in these products and increase the yield of high-quality products, some studies have employed dehydrochlorination catalysts in the reaction [12,13]. Iron oxide [14], calcium carbonate–carbon composites (Ca–C) [15], and red mud [16] are efficient chlorine sorbents for the dechlorination of decomposition products. In particular, iron oxide–carbon composites (Fe–C) are not only effective dechlorination catalysts, but are also effective chlorine sorbents [17]. The organic chlorine compounds that are observed during the thermal decomposition of waste plastics containing PVC are produced via two different routes: directly from the thermal decomposition of PVC, or as secondary products of the reaction between the hydrogen chloride generated and the PVC-derived organic compounds. The thermal decomposition of a mixture of PVC and polyethylene terephthalate (PET) yields characteristic chlorinated terephthalic acid derivatives [18]. Together these data imply that the contribution of the secondary reaction with hydrogen chloride is relatively large.

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0141-3910/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.polymdegradstab.2012.12.008

In our previous study, we examined the thermal decomposition of PVC in two different solvents to study the interaction between dechlorinated PVC and plastic-derived liquid products [19,20]. The distribution products from PVC depended on the solubility or hydrogen donability of the solvent, and the chlorine content in the products decreased linearly with the amount of transferred hydrogen from the solvent [21]. Here, we decomposed PVC in decalin or tetralin under high pressure of nitrogen to investigate the chlorination of the PVC-derived products or the organic solvent, because the secondary reaction with hydrogen chloride was expected to occur easily under high pressure.

2. Material and methods

2.1. Materials

Polyvinylchloride (PVC, 34675-6) was supplied by Sigma—Aldrich Co. LLC. Tetralin, decalin, and all organic chlorine compounds used as standards to identify compounds in the liquid product were purchased from Tokyo Chemical Industry, Co. Ltd. and were used without further purification.

2.2. Reaction procedures

Experiments were carried out in an autoclave (Hastelloy C, 200 ml) equipped a magnetic stirrer at 300–460 °C for 0–90 min under an initial nitrogen pressure of 4.0 MPa (Fig. 1). PVC (24 g) was charged into the autoclave with decalin (50 g) or tetralin. In all of the experiments, the autoclave was heated to the desired reaction temperature in 20 min and was quenched by blowing air after the reaction. Zero reaction time was defined to mean that the autoclave was quenched immediately after it reached the desired reaction temperature. Gaseous products were collected in an aluminum-ruminated gas bag through distilled water in a washing bottle to remove hydrogen chloride. Products were separated into the liquid product and vacuum residue by vacuum fractionation at 300 °C for 60 min.

2.3. Analytical procedures

Gaseous products were analyzed with an automatic gas chromatograph (Gasukuro Kogyo, GC-312). Hydrogen chloride absorbed in water was measured by ion-chromatography (Dionex, DX-AQ) with a packed column (IonPac AS12A). Liquid product was analyzed by a gas chromatography (Hewlett Packard: HP-5973, column: HP Ultra-1, 0.2 mm, 50 m) with a flame-ionized detector (FID) or a mass spectrum detector (MSD). Organic chlorine compounds in the liquid product were identified and quantified by a gas chromatography with an atomic emission detector (AED). We used 2-chloroheptan as an internal standard. The ratios of spectrum intensities of chlorine and carbon were used to measure the number of chlorine atoms contained in a molecule. Some pure organic chlorine compounds were used as internal standards to identify each chlorine compound in the liquid product.

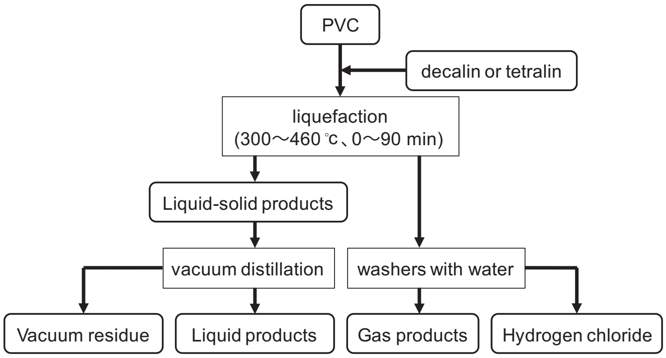

Fig. 1. Outline of the experimental procedure.

3. Results and discussion

3.1. Thermal decomposition of PVC in decalin

The distributions of products derived from the thermal decomposition of PVC in decalin at 300 °C and 400 °C are shown in Fig. 2 and Fig. 3, respectively. A relatively low yield of hydrogen chloride and high yield of vacuum residue was observed at zero time in the thermal decomposition of PVC at 300 °C. After 30 min, the yields of both products approached a constant, and the H/C ratio of the vacuum residue almost reached 1.0, which is the ideal value for the polyene chain derived from the dechlorination of PVC. These results indicate that the vacuum residue consisted mainly of a polyene chain and that the dechlorination of PVC was almost complete in 30 min at 300 °C. Slight further decomposition of the polyene chain to a liquid product or condensation to a solid residue was also observed.

The maximum yield of hydrogen chloride observed in the thermal decomposition of PVC at 400 °C implies that the dechlorination of PVC was compete in 30 min. Yields of the vacuum residue and the liquid product indicate that the vacuum residue further decomposed to the liquid product as the reaction proceeded. The finding that the H/C ratio of the vacuum residue was lower than 1.0 and continued to decrease as the reaction progressed indicates that the condensation reaction involving the polyene chain derived from the dechlorination of the PVC also occurred under these reaction conditions. The slight increase in vacuum

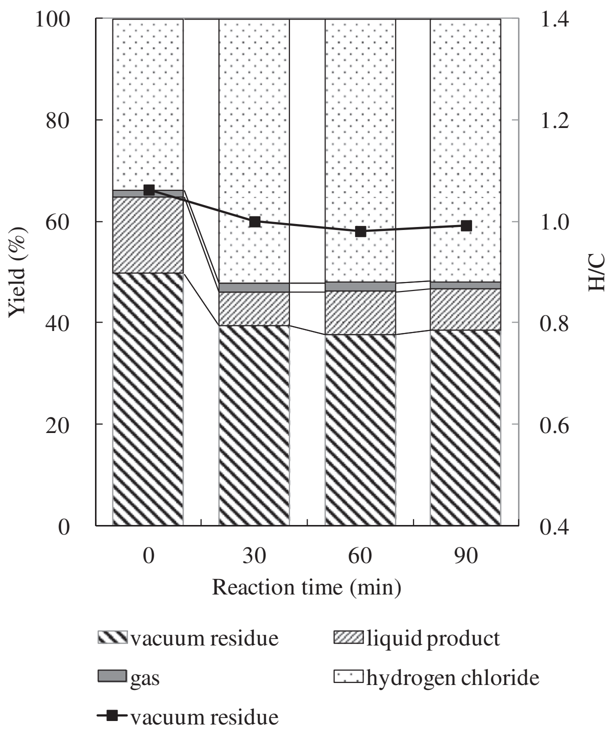

Fig. 2. Distribution of products derived from the liquefaction of PVC in decalin at 300 °C.