

## Research Article

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# Simple pyrolysis of polystyrene into valuable chemicals

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**Abstract:** Overuse of polymer products has led to severe environmental problems, which are threatening survival of creatures on earth. It is urgent to tackle enormous polymer wastes with proper cycling methods. Pyrolysis of polymers into high-value chemicals and fuels is displaying great potential to address the white pollution issue. In this study, we focus on chemical recycling of polystyrene, an important polymer in our everyday life, into valuable chemicals through simple pyrolysis strategy under nitrogen protection. It is found that yield of liquid product from polystyrene pyrolysis achieves as high as 76.24%, and there exists single component in the liquid product, which has been identified as styrene through hydrogen nuclear magnetic resonance spectra. Moreover, we propose monomer dissociation mechanism to explain the pyrolysis process of polystyrene based on the structure of polystyrene and experimental results.

**Keywords:** polystyrene, pyrolysis, styrene monomer, dissociation mechanism, chemical recycling

## 1 Introduction

Large-scale application of synthetic polymer products has greatly accelerated social development and improved everyday life of human society in past decades (1–3). But

excessive production of polymer products has given rise to severe environmental problems nowadays (4–6). The situation can be even worse in foreseen future because of the absence of effective tackling methods for waste polymers (7–9). Millions of tons of waste polymers produce every year, but are disposed inappropriately just by land-filling and incineration, which will lead to water, soil, and air contaminations (10,11). Even if functional polymers with novel properties for industrial applications are emerging one after another, effective disposal methods for waste polymers have not been put forward up to date (12–14). Since white pollutions have enormous negative influences on living of creatures on this planet, it is crucial to develop simple but effective strategy to realize chemical recycling of waste polymers without secondary pollutions.

Polymers mainly consist of long chains with repeated units in the structure and are usually chemically stable without any possibility to degrade into fragments by regular disposal methods (15–17). It seems to be an interesting strategy to pyrolyze waste polymers into valuable chemicals and fuels at high temperature under inert atmosphere (18–20). Polystyrene has become a common polymer that is utilized normally in everyday life, and there exist some companies for tackling polystyrene products. However, mainstream tackling method for waste polystyrene products is to recycle and reuse them. They collect waste polystyrene products and then clean them with solvents. After collecting and cleaning, these products are melted under high temperature and made into second-time products. But these recycled products always show deteriorated physical and chemical properties and are used in low-level scenarios. The pyrolysis method in this study can recycle waste polystyrene products without cleaning process, but directly obtain high-value styrene monomers. Large-scale applications at plant level have not been realized because of high energy cost, even if some companies have made some attempts previously.

In this study, we investigate pyrolysis methodology of waste polymers and take typical polystyrene as an example. Pyrolysis properties of polystyrene have been

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first studied by thermogravimetric analysis (TGA) technique and it is found that its optimal pyrolysis temperature should be 420°C under nitrogen atmosphere. The liquid product is the main product of polystyrene pyrolysis with a high mass-ratio yield of 76.24%, which consists of a single component with high percentage of 73%. According to the gas chromatography (GC) and nuclear magnetic resonance results, the single component has been identified as styrene monomers. In addition, a monomer dissociation mechanism has been put forward to address the pyrolysis process of polystyrene under inert atmosphere. This work provides a typical demonstration of chemical recycling method for waste polymers.

## 2 Experimental section

### 2.1 Materials

Polystyrene was obtained from Millipore Sigma company. Deuterated chloroform was bought from Sinopharm Chemical Reagent. Nitrogen ( $N_2$ ) was purchased from Praxair company.

### 2.2 Pyrolysis process of polystyrene

First, nitrogen was pumped into the pyrolysis system to remove air for 0.5 h. Second, 5 g polystyrene was put into crucible and continued to pump nitrogen for 10 min. Third, the pyrolysis system started to heat up to 420°C at heating rate of  $5^\circ\text{C min}^{-1}$  under nitrogen atmosphere. Finally, gas, liquid, and solid products were obtained after persistent pyrolysis at 420°C under nitrogen protection for 2 h.

### 2.3 Characterization

TGA of polystyrene was carried out on TA-Q50 instrument. GC characterization of liquid products was made

on CP3800 instrument. Hydrogen nuclear magnetic resonance (HNMR) analysis of liquid products was made on Bruker 400M NMR instrument.

## 3 Results and discussion

### 3.1 Chemical structure and pyrolysis process of polystyrene

In order to verify feasibility of pyrolysis method for chemical recycling of waste polymers, we utilized polystyrene, a common polymer in our everyday life, as a typical demonstration. Since the glass-transition temperature of polystyrene is as high as 100°C, polystyrene can be made into single-use containers for hot water and foods (21). Chemical structure of polystyrene is shown in Figure 1a, and its other information including formula, density, melting point, and solubility are also provided. In addition, schematic for the setup of polystyrene pyrolysis has been presented in Figure 1b. The pyrolysis process was protected by inert atmosphere (nitrogen in this work), whose flow rate was controlled by the flow meter in middle between gas container and pyrolysis reactor. A condenser with ice/water bath was set up after pyrolysis reactor for collection of liquid products from polystyrene pyrolysis. Gas phase products were taken out with nitrogen from the pyrolysis system, while solid phase products retained in the reactor.

### 3.2 Thermogravimetric analysis and pyrolysis products of polystyrene

To determine the optimal reactive conditions for pyrolysis of polystyrene materials, TGA of polystyrene has been carried out with heating rate of  $5^\circ\text{C min}^{-1}$  under nitrogen atmosphere. TGA technique is actually the simulation of polystyrene pyrolysis at very low massloading of sample

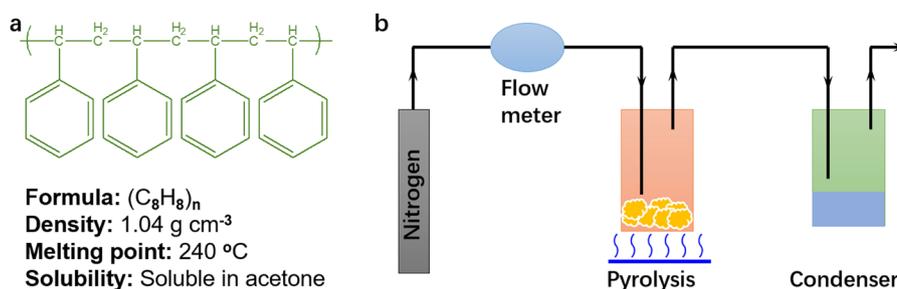
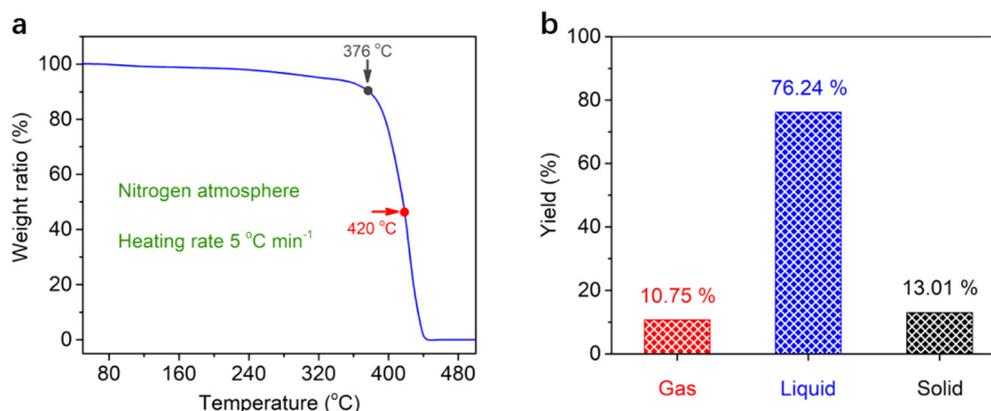


Figure 1: (a) Chemical structure of polystyrene. (b) Schematic for the setup of polystyrene pyrolysis.



**Figure 2:** (a) Thermogravimetric analysis of polystyrene. (b) Yield distribution of various products from pyrolysis of polystyrene.

and can directly provide valuable informations for practical pyrolysis with large massloadings (22,23). TGA result of polystyrene is presented in Figure 2a, which indicates that polystyrene starts to degrade at 376°C and then achieves its highest degradation rate at the temperature of 420°C. Based on pyrolysis results of polystyrene from TGA results, we employed the pyrolysis temperature of 420°C with heating rate of 5°C min<sup>-1</sup> under nitrogen atmosphere. Differential scanning calorimetry (DSC) can be utilized for detection of pyrolysis temperature, but its detection limit is below 300°C. Pyrolysis products of polystyrene mainly consist of three phases, including gas, liquid, and solid ones. The yield distribution of three products is displayed in Figure 2b, and the mass-ratio yields of gas, liquid, and solid products are 10.75%, 76.24%, and 13.01%, respectively. Liquid product is the main pyrolysis product, and thus is valuable for subsequent ingredient identification. It is possible to reduce pyrolysis temperature with catalysts, such as noble nano-metals, transition metal oxides, and zeolites.

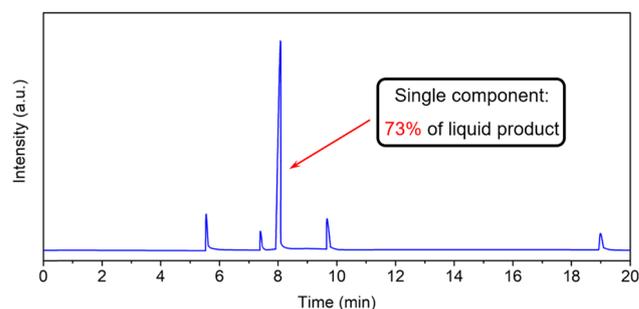
### 3.3 Gas chromatography spectra of liquid product from polystyrene pyrolysis

Since liquid product consists main pyrolysis products of polystyrene, it is essential to clarify the ingredient distribution of liquid product. To further identify the ingredient distribution of liquid product, GC characterization was adopted for analysis because of its high accuracy and good separating property for organic liquid samples (24,25). According to the GC spectra of liquid product in Figure 3, it is found that there exists a single component in liquid phase with a mass-ratio content as high as 73%. This result indicates that polystyrene materials can be

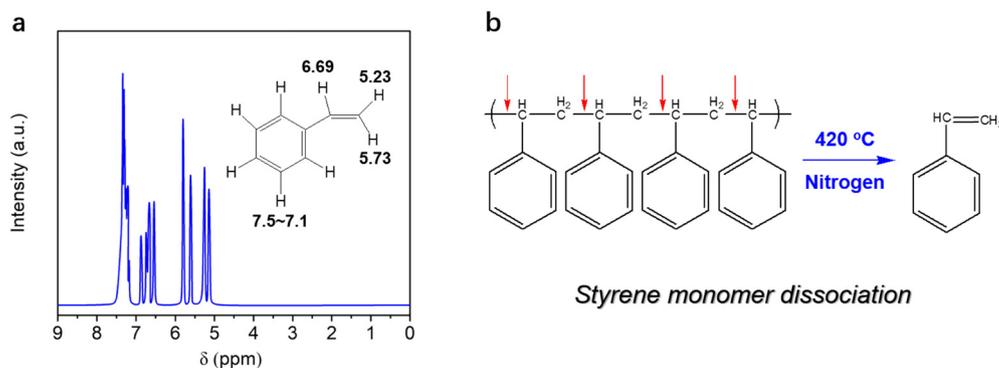
directly converted into liquid products with single component through simple pyrolysis, which has great potential for applications in chemical industry. And it is an important task to identify the chemical structure of single component, which can be realized through subsequent separation and purification processes with organic methods. This pyrolysis method can also be employed for other polymers, including polyethylene and polypropylene. But product distributions are different from polystyrene because of different pyrolysis mechanisms, which are determined by specific chemical structures.

### 3.4 Structure identification of single component in liquid product

The single component indicated by GC spectra can be separated and purified by distillation method under N<sub>2</sub> protection, and then identified with the aid of HNMR characterization. The HNMR spectra are shown in Figure 4a, which displays typical peaks which are the same with that



**Figure 3:** Gas chromatography spectra of liquid product from pyrolysis of polystyrene.



**Figure 4:** (a) HNMR spectra of the single component in liquid product from pyrolysis of polystyrene. (b) Styrene monomer dissociation mechanism of polystyrene pyrolysis.

of styrene monomers. The chemical shifts of different hydrogen atoms are analyzed and presented in the inset of Figure 4a. After analysis and comparison with standard spectra of styrene, it can be concluded that the single component in liquid product is styrene, which means that polystyrene intends to dissociate into styrene monomers under pyrolysis processes. It is worth mentioning that the recycled styrene has practical economic benefit and can be further utilized as valuable chemicals. In order to explain pyrolysis process of polystyrene, we propose a monomer dissociation mechanism as shown in Figure 4b. The polystyrene intends to degrade at the weak chemical bonds between  $\alpha$  hydrogen of one styrene unit and  $\beta$  hydrogen of next styrene unit. This is mainly resulted from the high stereo-hindrance effect of benzene rings in polystyrene structures, and thus it is very difficult to fracture between  $\alpha$  and  $\beta$  hydrogens in one styrene unit, finally leading to high pyrolysis selectivity of liquid products. This method shows potential for practical applications, but high energy cost should be alleviated for cost-effectiveness.

## 4 Conclusion

In this study, simple pyrolysis has been reported as an effective method for chemical recycling of polystyrene, which is a common polymer in human society. The optimal degradation temperature was investigated to be 420°C through TGA analysis. The pyrolysis products mainly consisted of three phases, including gas (10.75%), liquid (76.24%), and solid (13.01%) ones. We found that there existed single component (73%) in liquid product from polystyrene pyrolysis under nitrogen atmosphere, which was obtained from the analysis result of GC spectra.

It is clarified that the single component is styrene monomer identified from HNMR spectra of liquid product. Furthermore, we proposed a dissociation mechanism for explanation of polystyrene degradation at inert atmosphere under high temperature. The polystyrene chains prefer to degrade into monomers during pyrolysis processes owing to stereo-hindrance effect of benzene rings in the structure. The general research strategy is believed to be extended to other polymers, such as polyethylene, polydimethylsiloxane, and polyvinyl alcohol. We hope this study will shed light on chemical recycling of waste polymers.

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**Author contributions:** Chao Lu: writing – original draft, methodology, formal analysis; Hang Xiao: formal analysis, visualization; Xi Chen: writing – review and editing, project administration, resources.

**Conflict of interest:** Authors state no conflict of interest.

**Data availability statement:** All data generated or analyzed during this study are included in this published article.

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