

# TERTIARY RESOURCE RECOVERY FROM WASTE POLYMERS VIA PYROLYSIS: POLYPROPYLENE

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## ABSTRACT

Polypropylene is a significant component of mixed plastic waste from which fuels and chemicals can be recovered via thermal or catalytic degradation. Pyrolysis of polypropylene was investigated at a temperature of 420°C and reaction times ranging from 10 to 180 minutes. Total conversion reached approximately 60% at 90 minutes, and no significant change was observed for longer reaction times. The selectivity to monomer, propylene, achieved a plateau at approximately 10% after a reaction time of 90 minutes. The overall product distribution can be explained by the typical free radical mechanism with the dominant products as alkenes in the form of  $C_{3n}$ , alkanes in the form of  $C_{3n-1}$ , and dienes in the form of  $C_{3n-2}$ .

## I. INTRODUCTION

In recent years, post-consumer wastes have caused increased concern because of the escalation of municipal solid wastes (MSW) generated. In 1995, 208 tons of MSW were generated, and it increased to 340 tons in 1998, with more than 60% of MSW landfilled. The decreasing availability of landfill space and the inefficient use of post-consumer products through landfilling, have heightened the attention paid to recycling of MSW over the past decade.

Plastics make up a significant portion of post-consumer products. In the United States alone, over 70 billion pounds of plastics are manufactured annually, while only 10% of this amount is recycled or incinerated. In 1995, 9.1 weight percent of MSW was composed of plastics, with a total of 30% by volume. Among the plastic waste, 15.3 weight percent contained polypropylene.

Currently, the recycling of plastics can be divided into four categories - primary, secondary, tertiary, and quaternary. Primary recycling simply reuses the plastics as products that have similar properties to the discarded materials. Secondary recycling, also known as material or mechanical recycling, is achieved by melting, grinding, and reforming plastic waste mixtures into lower value products. Tertiary recycling converts discarded plastic products into high-value petrochemical or fuel feedstocks. Quaternary recycling uses combustion or incineration to recover energy from plastic products. Since primary and secondary recycling have limitations on the properties and uses of the final products, and quaternary recycling is an insufficient use of resources and has a negative public image because of release of  $CO_2$  and airborne particles, tertiary recycling promises the best long-term solution. However, tertiary recycling is not economical at present. One of the biggest costs is the sorting of the original polymers. Therefore, processing of multicomponent polymeric wastes may provide a potential solution. To establish a baseline to which pyrolysis of mixed plastic wastes containing polypropylene can be compared, the thermal degradation of neat polypropylene was examined.

## II. EXPERIMENTAL

Batch pyrolysis experiments were carried out by loading 20 mg of polypropylene (PP) into a 3.1-ml glass ampoule (Wheaton). The polypropylene was obtained from Aldrich Chemical ( $M_w=127,000$ ,  $M_n=54,000$ ) in powder form. After purging with argon for 2 minutes, each ampoule was sealed using an oxygen/propane flame, and then the sample was reacted in an isothermal fluidized sand bath at 420°C. Reaction times ranged from 10-180 minutes. Upon completion of the reaction, the ampoule was removed from the sand bath and quenched in another sand bath set at ambient temperature. Three replicates were performed for each reaction time.

Gaseous products were analyzed by putting the ampoule inside a 53-ml flask with a Tygon tube on one end and an injection port on the other. Both ends were then sealed with septa. The flask was purged with helium for 10 minutes and, after the ampoule was broken, allowed to equilibrate for 30 minutes. Two ml gas samples for the 10 minute reaction runs and 1 ml samples for the other runs were then taken using a gas-tight syringe. Gaseous products were then identified and quantified against known standards using a Hewlett Packard 5890 Series II Plus Gas Chromatograph equipped with a thermal conductivity detector (TCD) and a 6 ft stainless steel Porapak Q column (Supelco).

Liquid and solid products were extracted with 1.5 ml HPLC grade methylene chloride overnight. The product solution was first passed through a 0.45- $\mu$ m polypropylene filter (Alltech) attached to a syringe and then passed through a Waters Gel Permeation Chromatograph (GPC). Products with molecular weights less than ~400 g/mol were collected with the fraction collector attached to the GPC outlet. An external standard (biphenyl) was added after fraction collection. Product identification and quantification were achieved using a Hewlett Packard 6890 Series Gas Chromatograph-Mass Spectrometer and a Hewlett Packard 6890 Series Gas Chromatograph with a flame ionization detector (FID), each equipped with a Hewlett Packard 30 m crosslinked 5% Ph Me Silicone capillary column.

The percent conversion of PP, X, was defined according to the equation:

$$X = \frac{W_g + W_l}{W_o} \times 100\%$$

where  $W_g$  is the weight of gaseous products,  $W_l$  is the weight of liquid products with carbon number less than or equal to 25, and  $W_0$  is the initial weight loading of PP. Selectivity,  $S$ , of a certain species A was based on the following equation:

$$S = \frac{W_A}{W_g + W_l} \times 100\%$$

where  $W_A$  is the weight of species A. Product yields were normalized by dividing the millimoles of each product by the initial molar loading of polypropylene repeat units. Finally, error bars shown in the figures represent the standard deviations of experiments that have been triplicated.

### III. RESULTS

The overall conversion of neat pyrolysis of polypropylene increased with respect to reaction time, as illustrated in Figure 1. After 90 minutes of reaction, the conversion reached approximately 60%, and no significant change was observed at longer reaction times. This suggests that little additional conversion can be achieved even for very long reaction times at this temperature in a closed batch reactor of 3.1 ml. The selectivity of polypropylene monomer, propylene, showed similar behavior, achieving a selectivity of approximately 10% after 90 minutes of reaction as shown in Figure 2.

If the products were divided into three fractions,  $C_1$ - $C_4$ ,  $C_5$ - $C_{10}$ , and  $C_{11}$ - $C_{25}$ , respectively, the yields of these fractions behaved differently. As shown in Figure 3, the yield of the  $C_1$ - $C_4$  fraction increased with reaction time, whereas the  $C_5$ - $C_{10}$  fraction reached a maximum around 120 minutes and no significant change was observed at 180 minutes. Finally, the  $C_{11}$ - $C_{25}$  fraction reached a maximum around 60 minutes. These results suggest that as reaction time increased, the heavier products decompose to lighter ones.

The reaction products of polypropylene pyrolysis consisted of four major categories - alkanes, alkenes, dienes, and aromatic compounds. Lower molecular weight species were found in higher yields whereas there were notable decreases in the yields with carbon numbers greater than ten. For alkanes, the most dominant product was ethane ( $C_2$ ). In addition, pentane ( $C_5$ ), 4-methylheptane ( $C_8$ ),  $C_{11}$ ,  $C_{14}$ , and  $C_{17}$  were found in the highest yield; the alkanes were thus dominated by products with carbon numbers  $C_{3n-1}$ , with  $n=1, 2, 3, 4, \dots$ , as shown in Figure 4. The yields of the majority of the alkanes increased with respect to reaction time. For alkenes, propylene was the most dominant product with propylene oligomers ( $C_6$ ,  $C_9$ ,  $C_{12}$ ,  $C_{15}$ ,  $C_{21}$ , and  $C_{24}$ ), i.e.,  $C_{3n}$ ,  $n=1, 2, 3, 4, \dots$ , as the other major olefinic products. As shown in Figure 5, yields of alkenes with carbon numbers greater than five all reached maximum values then decreased when reaction time increased. However, yields of lighter alkenes (with carbon numbers less than five) increased monotonically with reaction time. Dienes, which were found beginning with  $C_7$  and were present in relatively low yields, appeared as  $C_7$ ,  $C_{10}$ ,  $C_{13}$ ,  $C_{16}$ ,  $C_{19}$ ,  $C_{22}$ , and  $C_{25}$ , i.e.,  $C_{3n-2}$ ,  $n=3, 4, 5, 6, \dots$  (not shown). They also appeared to reach maximum values then decrease except for  $C_7$ . Finally, aromatic compounds were also found as minor products. Their yields were comparable in magnitude to the diene yields. The yields of aromatic compounds generally increased with respect to reaction time (not shown).

As noted above, the product distribution showed that most alkenes appeared in the form of  $C_{3n}$ , whereas alkanes and dienes appeared in the form of  $C_{3n-1}$  and  $C_{3n-2}$ , respectively. This product distribution is in agreement with observations reported in the literature [1-2] and can be explained by the mechanism illustrated in Figure 6, which was based on the one proposed by Tsuchiya et al. [3]. The initiation step of the free radical mechanism is simply to break any of the PP long chains into two shorter end-chain radicals. The end-chain radicals (or mid-chain radicals formed subsequently) may abstract hydrogen from a PP long-chain to form a tertiary radical, as shown in Figure 6(a). Upon undergoing  $\beta$ -scission, the tertiary polymer radical is broken into two parts, one with a double bond on the end (denoted as I), and the other with a secondary free radical (denoted as II). When the polymer chain I is attacked by another free radical and  $\beta$ -scission occurs, dienes (in the form of  $C_{3n-2}$ ) and alkenes (in the form of  $C_{3n}$ ) can be formed, as shown in Figure 6(b). On the other hand, polymer chain II can undergo three kinds of reactions such that alkanes (in the form of  $C_{3n-1}$ ) and alkenes (in the form of  $C_{3n}$ ) can be formed. Figure 6(c) shows three possible reaction pathways of polymer chain II. Although other steps not explicitly drawn are possible, the formation of  $C_{3n}$  alkenes,  $C_{3n-1}$  alkanes and  $C_{3n-2}$  dienes as the dominant products suggests that the mechanism in Figure 6 captures the major reaction pathways.

### ACKNOWLEDGMENT

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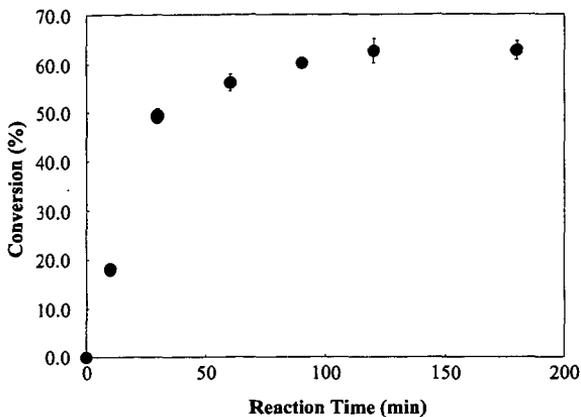


Figure 1 : Conversion of polypropylene as a function of reaction time.

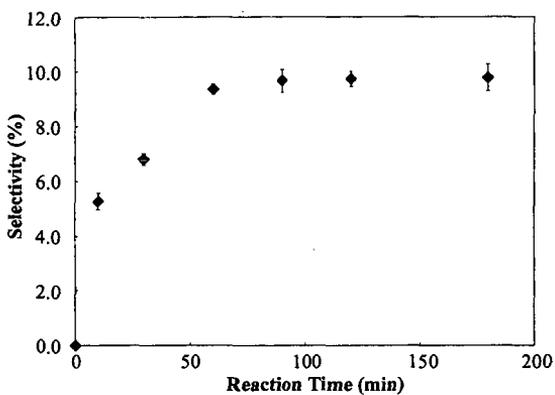


Figure 2 : Selectivity of propylene as a function of reaction time.

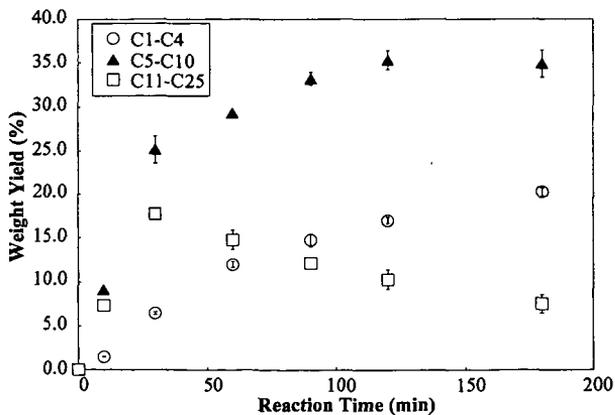


Figure 3 : Weight yields of different product fractions as a function of reaction time.

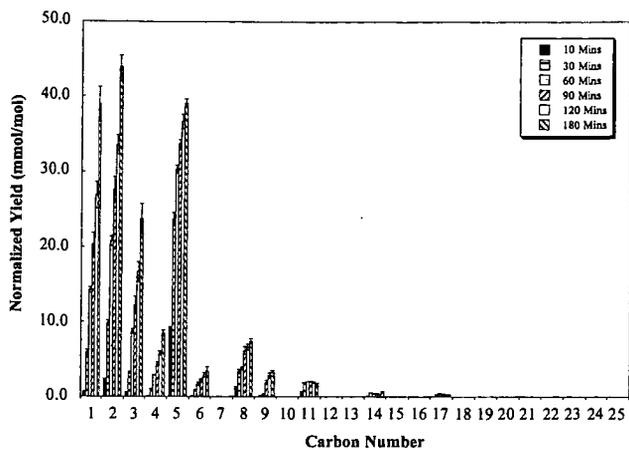


Figure 4 : Comparison of normalized yields of alkanes as a function of reaction time and carbon number.

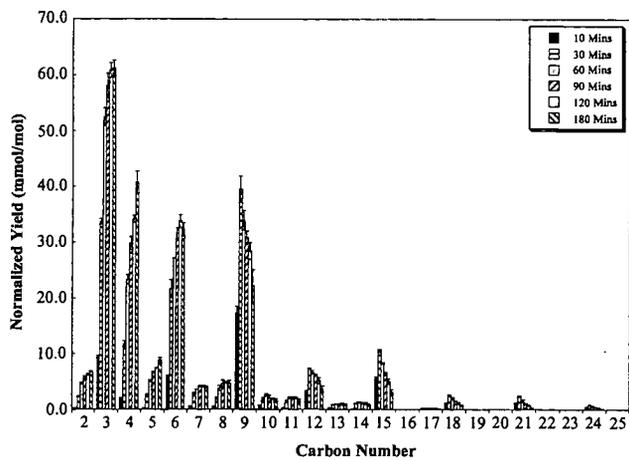


Figure 5 : Comparison of normalized yields of alkenes as a function of reaction time and carbon number.

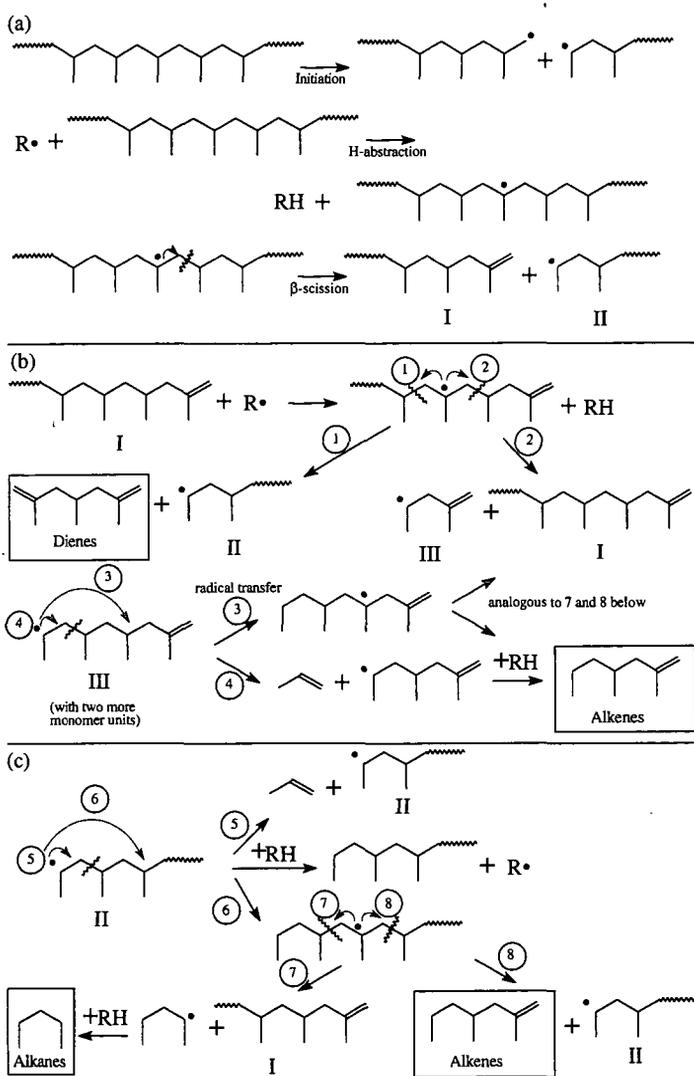


Figure 6: (a) Formation of two kinds of polymer chains (I and II) through bond fission, hydrogen abstraction and  $\beta$ -scission and proposed reaction mechanisms of polymer chains (b) I and (c) II.