Chemical Engineering Journal 98 (2004) 53–60

Chemical Engineering Journal

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Pyrolysis characteristics of polystyrene and polypropylene in a stirred batch reactor

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Received 22 February 2003; accepted 21 June 2003

Abstract

Kinetic tests on pyrolysis of polystyrene (PS) and polypropylene (PP) were carried out with a thermogravimetric analysis (TGA) technique at the heating rate of 0.5, 1.0, and 2.0 °C min^{-1} in a stirred batch reactor. The polystyrene was mainly decomposed between 370 and 410 °C at the heating rates, whereas the polypropylene between 400 and 460 °C. The apparent energy of activation and the apparent order of reaction were determined at conversions from 1 to 100%. The ranges of apparent energies of activation of polystyrene were from 164 to 249 kJ mol^{-1} at conversions in the range of 1–100% and the apparent order of reaction was 0.32. The apparent energies of activation of polypropylene increased slowly from 208 to 288 kJ mol^{-1} and the apparent order of reaction was 0.01. The effects of heating rate on the product distribution have been studied. The selectivity of hydrocarbons corresponding to the styrene monomer and dimer was very high for the pyrolysis of polystyrene. The selectivity of specific hydrocarbons, however, was not observed for the case of polypropylene.

Keywords: Pyrolysis; Polystyrene; Polypropylene; Stirred batch reactor; TGA; Carbon number distribution

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1. Introduction

Continuous accumulation of waste plastics leads to serious problems all over the world. Most of the waste plastics have been landfilled in Korea. The landfill of combustible waste including plastics in Korea, however, will be prohibited in the near future. Recycling of waste plastics has recently received significant attention all over the world. Utilization of waste plastics as fuels or chemicals is a more attractive way for recycling the waste plastics. The pyrolysis of waste plastics could play an important role in converting this waste into economically valuable hydrocarbons, which can be used either as fuels or as feed stock in the petrochemical industry. Pyrolysis studies have been widely used for converting solid fossil fuels and organic materials such as coal [1,2], used tire [3,4], waste plastics [5–15], waste cellulose materials [16,17], waste lubricating oil [18–20] and oil shells [21,22] into liquid and gaseous hydrocarbons and a solid char residue.

Polystyrene (PS) is characterized by great rigidity, high surface gloss and excellent transparency. It is very easy to process PS, because of its good flow properties. Therefore, PS has widely been used for various purposes [23]. Polypropylene (PP), with the wide range of properties, has been applied to extremely versatile materials. It can be made flexible or very stiff, tough or very strong, transparent or opaque. PP is used for a huge variety of applications: fibers, tapes, film and sheet, board, tubes and blow moldings, and for all sort of injection molded parts [23].

Numerous studies for PS and PP have been conducted to maintain the environmentally compatible economic growth and to determine the kinetics of thermal degradation [5–14,24–30]. Some studies have been reported to elucidate the mechanism of polystyrene degradation. Carniti et al. [9] proposed that thermal degradation of polystyrene to volatile products be interpreted by the following consecutive reactions in tubes sealed under vacuum:

$$\text{PS (and heavy products of partial degradation)} \rightarrow C_{13}\text{–}C_{24} \rightarrow C_6\text{–}C_{11}$$

Sato et al. [7] investigated reaction properties of the thermal degradation of PS in solution using several solvents, and a mechanism for the reaction was proposed to explain these properties. Ranzi et al. [29] studied a mechanistic kinetic model able to describe the radical chain pyrolysis reactions taking place in the liquid phase for polyethylene and polypropylene.

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doi:10.1016/S1385-8947(03)00184-0

Nomenclature

A	preexponential factor (s^{-1})
E	activation energy (kJ mol^{-1})
k	pyrolysis rate constant (s^{-1})
n	reaction order
R	gas constant = 8.314 kJ kmol^{-1} K^{-1}
t	pyrolysis time (s)
T	pyrolysis temperature (K)
W	weight of sample at time t (g)
W_0	initial weight of sample (g)
W_∞	final weight of sample (g)
X	conversion of sample material

Greek letter

β	heating rate (°C min^{-1})

The main purpose of this work is to determine the global kinetic parameters during the non-isothermal pyrolysis of PS and PP. In this study, the pyrolysis of PS and PP was investigated by using a new and highly efficient technique. A TGA technique was applied to the pyrolysis in a stirred batch reactor and the global pyrolysis kinetic parameters were studied. The effect of heating rate on carbon number distributions of products was investigated.

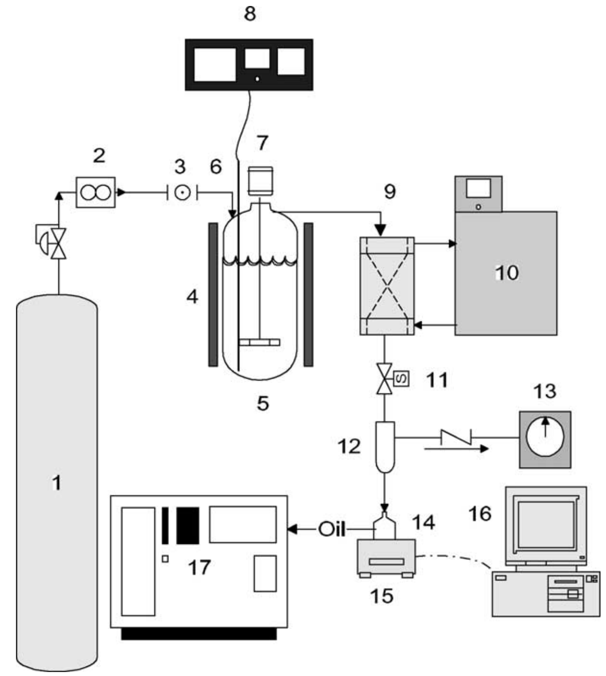

Fig. 1. Schematic diagram of pyrolysis reactor. 1: Nitrogen bomb; 2: flowmeter; 3: balb valve; 4: heater; 5: pyrolysis reactor; 6: thermocouple; 7: strirrer; 8: temperature, pressure and rpm controller; 9: condenser; 10: circulator; 11: solenoid valve; 12: cylinder; 13: wet gas meter; 14: reservoir; 15: balance; 16: computer; 17: GC.

2. Experiment

A schematic diagram of the autoclave (R-201, Reaction Engineering) for the pyrolysis of PS and PP is shown in Fig. 1. The pyrolysis of PS and PP was carried out in a stirred batch reactor, and the experiment was operated at an atmospheric pressure. The experimental apparatus is characterized as a semi-batch operation, because pyrolyzed products are evolved continuously during the course of the reaction. The cylindrical pyrolysis reactor of stainless steel has a volume of 1000 cm^3. The reactor was equipped with a mechanical agitator to minimize the temperature profile in the reactor. The temperature of the pyrolysis reactor was adjusted by means of a PID temperature controller equipped with a programmable device. A standard thermocouple (chromel–nickel) was installed into the sample material to provide an accurate temperature of the sample during the analysis. This procedure allowed the temperature of the sample to be registered at every moment, and the inaccuracy of the measurements caused by the temperature gradient was minimized.

Table 1 shows the characteristics of the sample used in this study. The properties of the sample were characterized by DSC (Perkin-Elmer 7 Series Thermal Analysis System). The results of elemental analysis of PS and PP are given in Table 2.

A sample mass of 300 g was employed for all experimental runs. To make an oxygen-free atmosphere, nitrogen was introduced into the reactor at a large rate of flow; then the nitrogen was cut off and the mixing rate was set at 100 rpm throughout the experiment. The heating rate was controlled at 0.5, 1.0, or 2.0 °C min^{-1} in order to heat up the pyrolysis temperature from 300 to 500 °C. At temperatures below 300 °C, the heating rate was controlled 10 °C min^{-1} because PS and PP did not decompose under 300 °C. The deviation of temperature in the reactor was ±1 °C for the pyrolysis temperature of 300–500 °C. The

Table 1
Properties of polystyrene and polypropylene

	$\bar{M}_w$	$\bar{M}_n$	T_g (°C)	ΔC_p (J g^{-1} °C^{-1})	T_m (°C)	ΔH_m (J g^{-1} °C^{-1})
PS[a]	313700	169500	101.48[b]	0.29[b]	–	–
PP[c]	209200	52800	–	–	165.11[b]	107.29[b]

[a] Hannam Chemical Co. [GP-150].
[b] Measured by DSC [Perkin-Elmer 7 Series Thermal Analysis System].
[c] Daelim Poly Co. [PP-137].

Table 2
Elemental analysis of polystyrene and polypropylene

	Element (wt.%)				H/C ratio
	C	H	N	S	
PS	91.60	8.07	–	0.15	1.06
PP	85.52	14.40	–	0.31	2.03

decomposed gas was condensed with cooling fluid at a temperature of 0 °C in the condenser. The cooling fluid was made up of the mixture of ethanol and deionized water. The yields of liquid pyrolysis products were determined gravimetrically by weighing condensed liquid product, while the volume of uncondensed gases was determined by using a wet gas-meter. The experimental data were recorded on a personal computer during the entire period every 10 s. The liquid products were analyzed by gas chromatography with a flame ionization detector (Young Lin-M600D). A capillary column HP-1 of 0.53 mm i.d, and 5 m length was employed. The peaks were identified by matching retention times with reference compounds (ASTM, 1995) [31].

3. Results and discussion

3.1. Thermogravimetric analysis results

For all thermogravimetric experiments, the results are expressed as a function of the degree of conversion X, which is defined as:

$$X = \frac{W}{W_0 - W_\infty} \tag{1}$$

where W_0 is the initial mass of sample, W the mass of product oil and W_∞ is the final residual mass corresponding to that of solid by-products including unpyrolyzed sample. When PS and PP are pyrolyzed (i.e. heating to ∼500 °C), PS and PP decomposes to yield an oil, gas and solid by-products. As mentioned in the experimental section, the condenser temperature was maintained at 0 °C to condense the products. For the pyrolysis of PS at the heating rates used here, the effluent gas from condenser was not detected with wet gas-meter. The result reveals that the benzene does not decompose in the repeating unit of PS under 500 °C. Likewise, the effluent gas was not detected when PP was pyrolyzed in the stirred batch reactor. In our previous work, waste automobile lubricating oil was pyrolyzed in the same conditions [18]. In that case, The volume of gas was in the range of 0.87–2.81 l for 0.5–2.0 °C min^{-1} and that of produced oil was 91.64–93.28 wt.%. In the case of PS and PP, the hydrocarbons under C_4 did not detect by wet gas-meter. The produced oil for the pyrolysis of PS and PP was 92.30–94.21 wt.%. Therefore, mass balance was evaluated as the difference with the mass of the reactants PS and PP, the mass of the produced oil, and the residual mass in the reactor bottom.

Fig. 2 shows the degree of conversion versus temperature for dynamic experiments at the different heating rate of 0.5, 1.0 and 2.0 °C min^{-1}. The decomposition of PS was initiated at a lower temperature with the comparison of PP. The pyrolysis of PS was initiated at the temperature of 360, 370, and 384 °C, respectively, at the heating rates of 0.5, 1.0, and 2.0 °C min^{-1}. PP was pyrolyzed at the temperature of 387, 405, and 411 °C at the heating rates of 0.5, 1.0, and 2.0 °C min^{-1}. The decomposition patterns of PS were more rapid in comparison with those of PP at the thermogravimetric curves. These results mean that PS decomposes in the temperature of narrow range. At the heating rate of 0.5 °C min^{-1} of PS and PP, it can be observed that the degree of conversion increased sharply until $T = 400$ °C (PS; $X = 0.90$) and $T = 440$ °C (PP; $X = 0.94$), respectively. At temperatures above 400 and 440 °C, the curve has a smooth slope and tends asymptotically to the maximum degree of conversion. All three heating rates exhibited the same patterns of thermal decomposition. These results indicate that PS and PP are pyrolyzed in one stage at the temperature range of 300–500 °C in the stirred batch reactor.

3.2. Rate of reaction

An instantaneous rate of conversion, dX/dt is obtained from the curve in Fig. 3 at the given reaction temperature. One maximum rate of conversion occurs at a specific reaction temperature for each heating rate. As shown in Fig. 3, the increase in the heating rate shifted the rate curve and the maximum rate of dX/dt to the higher temperatures. As the heating rates increased, the higher instantaneous thermal energy is released into the reaction system and results in higher rate of conversion. The results of Fig. 3 also indicate that the larger fraction of PS and PP are pyrolyzed in the reaction temperature range of 370–460 °C. The maximum rate of PS occurred at 376, 391, and 400 °C and PP was 407, 423, and 431 °C for heating rate of 0.5, 1.0, and 2.0 °C min^{-1}, respectively. The rate of weight variation was shifted lateral with the increase of heating rates. The lateral shift to higher temperatures for the maximum region of weight variation was also observed by other workers. For example, Liou et al. [17] showed a lateral increase in the maximum rate of weight change of 20 °C, as heating range was increased from 2 to 5 °C min^{-1} for acid-leached rice husk. In my previous work, the lateral shift to higher temperature with the increasing of heating rate showed for the pyrolysis of waste automobile lubrication oil [18].

3.3. Activation energy

Thermogravimetric analysis (TGA) for the differential method and for the integral method has been extensively studied by other researchers [32–36]. The derivation of pyrolysis kinetic data in this work applied the differential

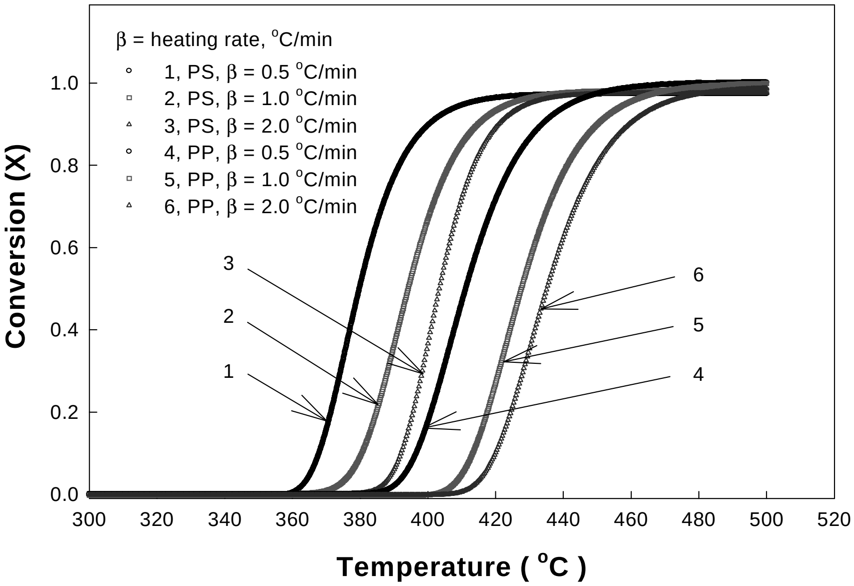

Fig. 2. The effect of pyrolysis rate of polystyrene and polypropylene on heating rate.

method. The rate of conversion, dX/dt, in thermal decomposition is expressed by:

$$\frac{\mathrm{d}X}{\mathrm{d}t} = kf(X) \tag{2}$$

The reaction rate constant k is expressed by the Arrhenius equation:

$$k = A\exp\left(\frac{-E}{RT}\right) \tag{3}$$

A function of conversion independent of temperature, $f(X)$, is expressed as:

$$f(X) = X^n \tag{4}$$

Substituting Eqs. (3) and (4) into Eq. (2) and taking a natural logarithm, the above equation yields:

$$\ln\left(\frac{\mathrm{d}X}{\mathrm{d}t}\right) = \ln(AX^n) - \frac{E}{R}\frac{1}{T} \tag{5}$$

Apparent energy of activation E, based on Eq. (5), is determined from a relationship between ln(dX/dt) and 1/T. Thus, a family of parallel straight lines of slope $-E/R$ is obtained. The apparent energy of activation (E) corresponding to the selected conversion is obtained. For example, when the conversion of PS was 10%, temperatures were 367.83, 380.33, and 392.0 °C with the heating rate of 0.5, 1.0 and 2.0 °C min^{-1}, respectively. The values of ln(dX/dt) were 2.98, 3.41, and 4.30, with corresponding values of 1/T

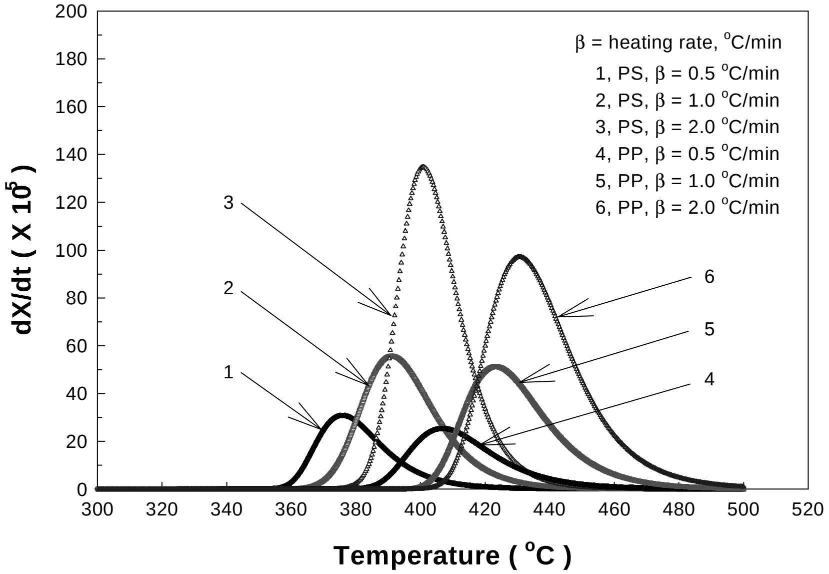

Fig. 3. Variation of the instantaneous reaction rate with temperature at different heating rates for pyrolysis of polystyrene and polypropylene.

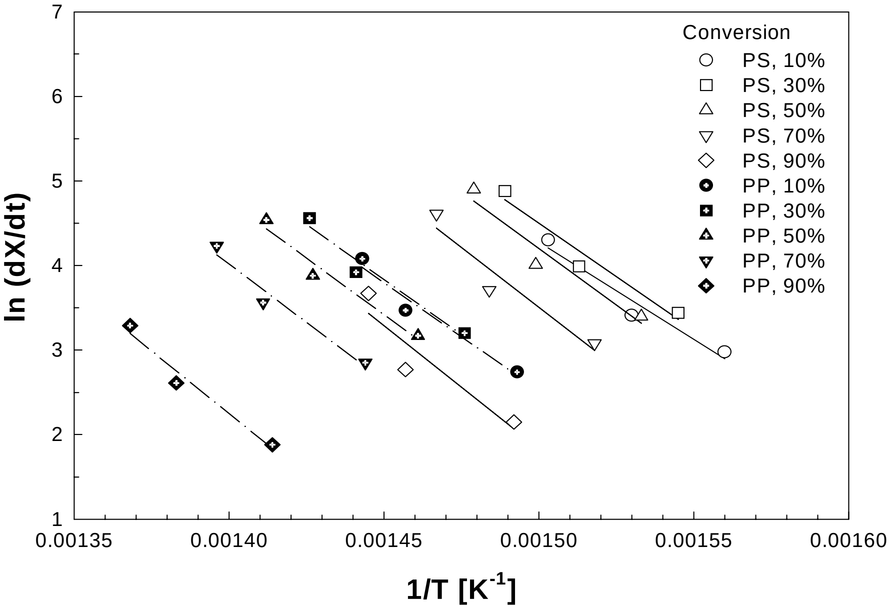

Fig. 4. Application of Eq. (5) with heating rate of 0.5, 1.0 and 2.0 °C min^{-1} for polystyrene and polypropylene. The conversion values are 10, 30, 50, 70 and 90%.

(K^{-1}) at 1.560×10^{-3}, 1.530×10^{-3}, and 1.503×10^{-3}. Fig. 4 was shown like the following for PS and PP: $\ln(\mathrm{d}X/\mathrm{d}t)$ as a y-axis and $1/T$ (K^{-1}) as an x-axis at conversions of 10, 30, 50, 70, and 90%.

The intercept ($\ln(AX^n)$) can be calculated from Fig. 4 at each conversion. The apparent order of reaction (n) and the pre-exponential factor (A) are obtained by curve fitting based on Eq. (6):

$$\ln(AX^n) = \ln A + n \ln(X) \qquad (6)$$

The variations of apparent energies of activation as a function of conversion are presented in Fig. 5. The greater apparent energy of activation was observed in the later period of the conversions. The range of apparent energies of activation of PS was between 164 and 249 kJ mol^{-1}, and PP was between 208 and 288 kJ mol^{-1}. PS and PP are highly branched with an aromatic ring and a methyl group in its repeating units. In the case of PS, due to the stability of the aromatic ring in aromatics molecules, the aromatic ring is not easy to rupture at low temperature under 500 °C, and it

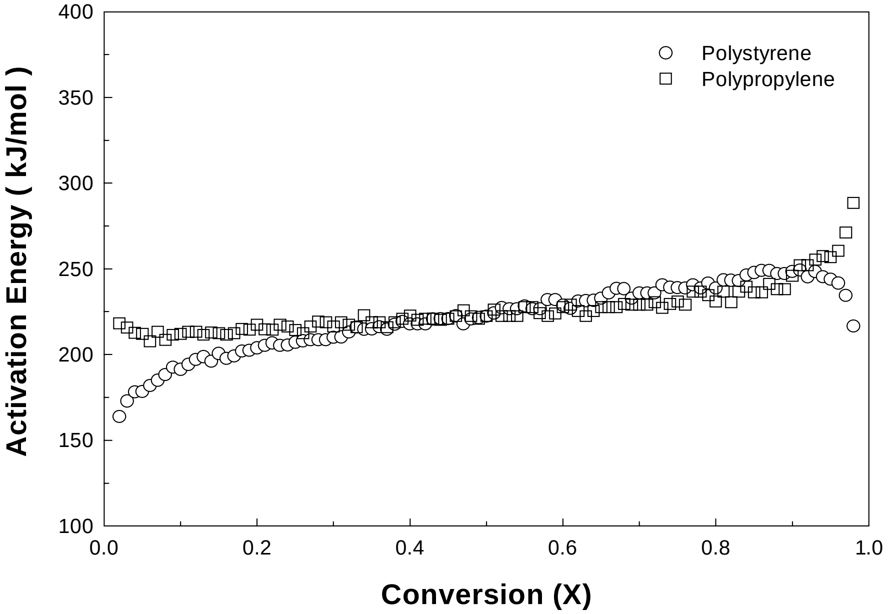

Fig. 5. Calculated activation energies at different conversions for pyrolysis of polystyrene and polypropylene.

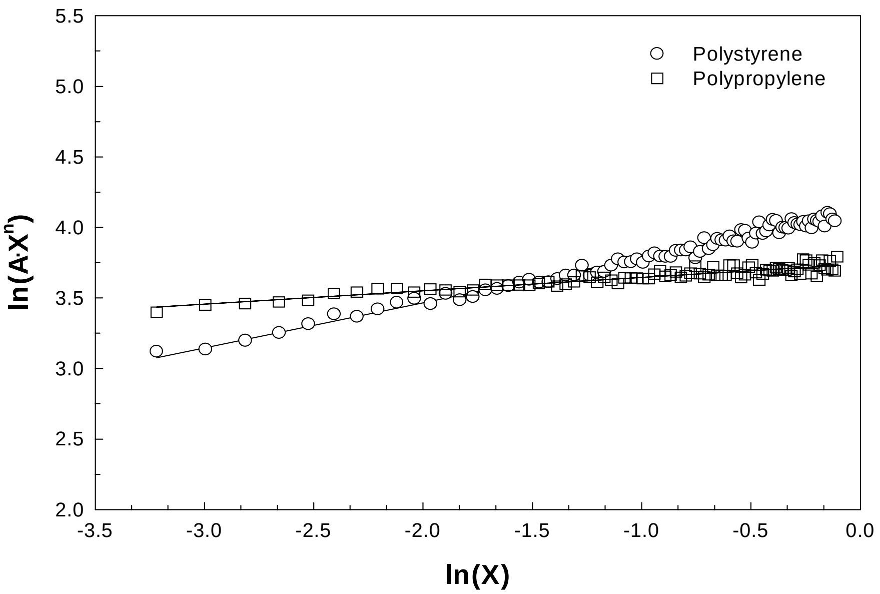

Fig. 6. The overall reaction order for pyrolysis of polystyrene and polypropylene.

remains unchanged. At low conversions, the decomposition of PS proceeds to cut the aromatics in its repeating units, and then the breaking of C–C bonds included in the main chain decomposes with the increase of conversions. That is, as the conversions increased, *E* also increased and seemed to be approaching relatively stronger chemical bond dissociation energy. It is showed that the width of apparent energy of activation was similar to the PS and the PP. Westerhout studied the pyrolysis of HDPE, LDPE, PP and PS using a TGA in the temperature range of 365–450 °C [5]. They reported that the pyrolysis rate increased in the following order: HDPE $<$ LDPE $<$ PP $<$ PS, which implies that the pyrolysis rate increases to the extent of branching. This means that the polymer having a side chain decomposes at low temperature and the apparent energy of activation is relatively low. In the same experimental conditions, we ran experiments for waste automobile lubricating oil. Waste automobile lubrication oil chains are not branched at all. The apparent energy of activation of waste automobile lubricating oil was between 282 and 448 kJ mol^{-1} [18]. The pyrolysis rate increased in the following order: waste automobile lubricating oil $<$ PP $<$ PS.

In order to obtain the order of reaction, plotting of data is shown in Fig. 6. Fig. 6 shows such linear relations that the apparent order of reaction (*n*) of 0.32 and 0.01 is determined for PS and PP, respectively. The average activation energy (*E*), overall order of reaction (*n*), and pre-exponential factor (*A*) are listed in Table 3.

4. Analysis of product oil

To analyze the reaction products, the samples were dissolved in CS_2. Pyrolyzed oil was quantitatively determined by GC. The product distributions of PS and PP in terms of carbon number obtained at different heating rates are shown in Fig. 7. As shown in Fig. 7, the major products of PS were the group of styrene monomer and dimer hydrocarbons, which involved one aromatic and two aromatics. Other products such as styrene trimer were formed to only a limited extent. The content of styrene trimer shifted slightly to higher hydrocarbons with the increase of heating rates. These results suggest that the increase of heating rate results in shorter retention. Therefore, the energy required for decomposition of organic matter decreases, which causes carbon numbers to increase. As mentioned in the introduction section, Carniti et al. [9] proposed that PS be decomposed by the consecutive reactions with two steps. From the analysis of carbon number distribution, it is thought that his proposal seems to be reasonable for the pyrolysis of PS.

Table 3
Kinetic parameters of PS and PP

Authors	*T* (°C)	*X* (wt.%)	*n*	*A*	*E* (kJ mol^{-1})
Kim et al. (waste lubricating oil)	300–500	0–100	1.35	334.29	282–448 (334)
This study (polystyrene)	300–500	0–100	0.32	60.6	164–249 (221)
This study (polypropylene)	300–500	0–100	0.01	42.08	208–288 (221)

The values in parentheses are average values.

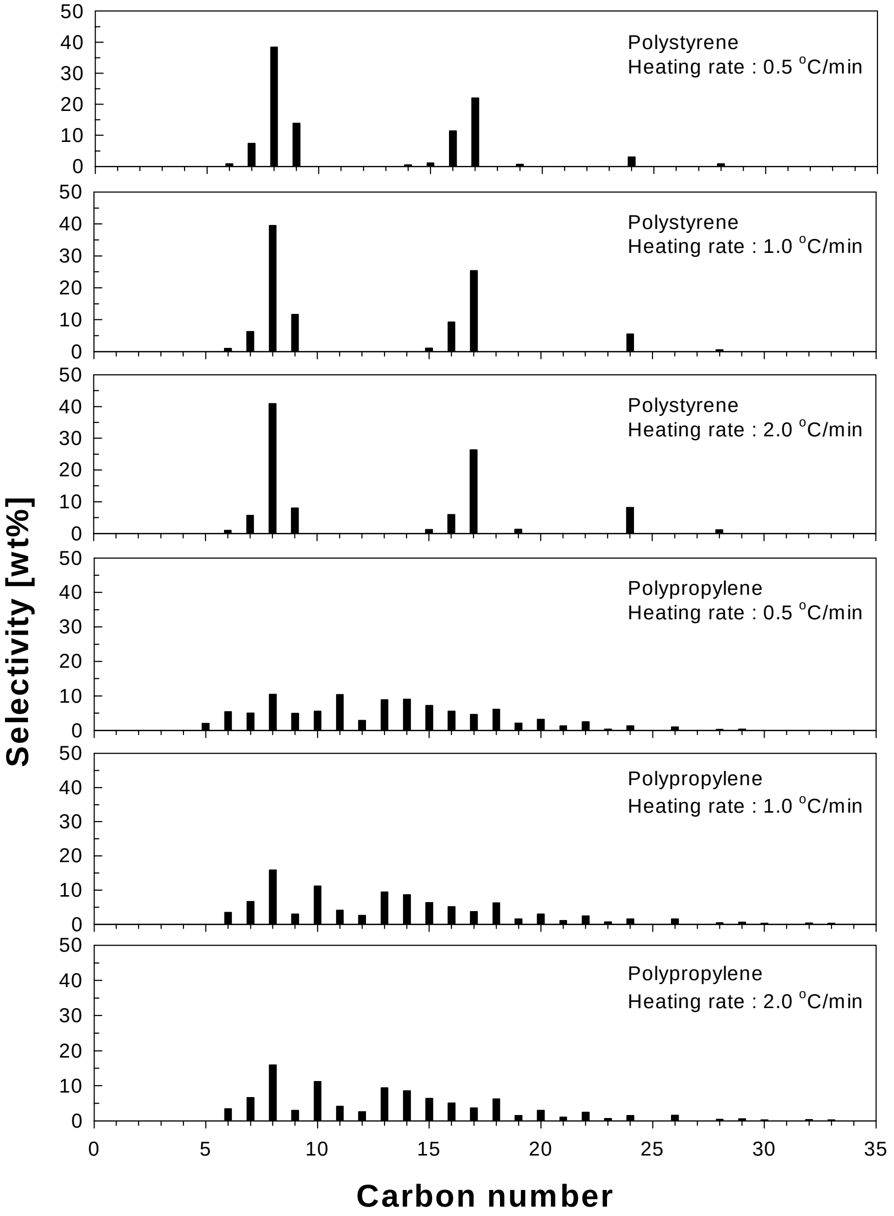

Fig. 7. The effect of heating rate on carbon number distribution for polystyrene and polypropylene.

There was not a specific characteristic for the pyrolyzed products of PP in contrast with the case of PS. The light hydrocarbons increased slightly with the decreasing of heating rates. These results suggest that the decrease in heating rate results in longer retention. Therefore, the energy required for decomposition of organic matter increases, which causes light hydrocarbons to increase.

5. Conclusions

Kinetic tests on pyrolysis of polystyrene and polypropylene were carried out using a thermogravimetric analysis technique at the heating rate of 0.5, 1.0, and 2.0 °C min^{-1}. The apparent energy of activation and the apparent order of reaction were determined at conversions from 1 to 100%. The apparent energies of activation increased with the increase of conversions. The ranges of apparent energies of activation of PS were from 164 to 249 kJ mol^{-1} at conversions in the range of 1–100% and the apparent order of reaction was 0.32. The apparent energies of activation of polypropylene increased slowly from 208 to 288 kJ mol^{-1} and the apparent order of reaction was 0.01.

Each carbon number distributions of the produced oil at a different heating rate were analyzed. The selectivity of hydrocarbons corresponding to the styrene monomer and dimer was very high for the pyrolysis of PS, while the selectivity of specific hydrocarbons was not observed for the PP. The carbon number distribution of produced oil shifted slightly to light hydrocarbons with a decrease in heating rates. The result shows that the energy to decompose the organic matter increases with increasing the retention.

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