On the Intrinsic Reaction Kinetics of Polypropylene Pyrolysis

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Abstract. The growing global plastic waste challenge requires the development of new plastic waste management strategies such as pyrolysis that will enable a circular plastic economy. Pyrolyzed plastics thermally convert into a complex mixture of intermediates and products that includes their constituent monomers. Developing optimized, scalable pyrolysis reactors capable of maximizing the yield of desired olefinic products requires a fundamental understanding of plastic pyrolysis mechanisms and reaction kinetics. Accordingly, the intrinsic reaction kinetics of polypropylene (PP) pyrolysis have been evaluated by the method of Pulse-Heated Analysis of Solid Reactions (PHASR), which enables the time-resolved measurement of pyrolysis kinetics at high temperature absent heat and mass transfer limitations. The yield of gas chromatography-detectable light species ($<C_{20}$) and the total yield of volatile products were quantified at five temperatures (525, 550, 575, 600, and 625 °C) for reaction times of 20 ms to 2.0 s, generating polypropylene pyrolysis product evolution curves that were compared to literature data. The overall reaction kinetics were described by a lumped first-order consumption model with an activation energy of 242.0 \pm 2.9 kJ mol⁻¹ and a pre-exponential factor of 35.5 \pm 0.6 ln(s⁻¹). Additionally, the production of the solid residues formed during polypropylene pyrolysis was investigated, revealing a secondary kinetic regime.

1.0 Introduction. Plastics are ubiquitous materials owing to their unique combination of useful material properties and affordability. Since the 1950s, industrial-scale production of plastics has grown from an estimated two million metric tons (Mt) annually to approximately 438 Mt as of 2017.¹ Based on current trends, the annual rate of plastic production is projected to exceed one billion tons by 2050.1 This massive growth in plastic production has resulted in the generation of an immense amount of plastic waste, particularly due to the large fraction of plastics being produced for singleuse applications, such as packaging.² As of 2017, approximately 7000 Mt of plastic waste has been generated and it is projected that this cumulative quantity will grow to 33,000 Mt by 2050.¹ Effective waste management strategies must be developed to manage existing and future plastic waste. Polypropylene (PP) is particularly important to the plastic waste problem; PP is the most widely produced thermoplastic material accounting for around 17% of annual global plastic production, 18% of plastic packaging, and 24% of plastics in municipal solid waste.^{1,3–5}

End-of-life (EOL) plastics that have exceeded their useful product life have been conventionally considered waste products. EOL plastics are primarily discarded in landfills, accumulating as plastic waste.^{1,6} As of 2017, 76% of all plastic waste generated was discarded, 14% was incinerated, and only 10% was recycled.¹ While incineration allows for energy recovery and prevents the accumulation of plastic waste, it still leads to the release of CO₂ and other environmental toxins (e.g., dioxins) and prevents the reuse of plastics.^{6–8} Recycling offers a route through which the plastics can be reused, but traditional mechanical recycling is incapable of converting plastics back to their original form. The methods involved with thermomechanical processing (e.g., remelting and pelletizing) result in the degradation of the plastic material, requiring the addition of



Figure 1. Polypropylene pyrolysis network. Polypropylene undergoes primary (solid blue pathways) thermal conversion via radical reactions to produce solid, liquid, and gaseous products which may undergo secondary and higher-order reactions (red dashed pathways).

virgin plastics to improve material properties; alternatively, these can be downcycled and eventually discarded.^{6,8,9} Mechanical recycling is also sensitive to mixed waste streams and impurities, leading to reductions in material quality and increased costs.^{6–10} Continued use of these traditional waste management strategies fails to address the global plastic waste problem.

Chemical recycling provides an alternative approach to plastic waste management in a circular economy in which EOL plastics are viewed as a resource, rather than a waste product, to produce new plastics and chemicals.^{6–9,11} Many chemical recycling processing options exist including pyrolysis.^{8,9,12–14} solvolvsis. hydrolysis, and Pyrolysis is the thermal conversion of a material in an inert oxygen-free environment to produce a variety of liquids and gases, including plastic monomers; this processing method can accommodate highly heterogenous and contaminated plastic waste streams, making it more cost-effective at scale.^{3,9,10,15}

The chemistry of polypropylene pyrolysis is highly complex, involving many intermediates and products. A detailed description of the reaction network and associated reaction kinetics that matches experimental data does not yet exist, with existing models being incompletely described by empirical formulas or sets of elementary steps.^{16–20} **Figure 1** illustrates several groups of the many reaction pathways and products that have been reported for polypropylene pyrolysis.^{19–70} While there is not yet a complete understanding of polypropylene pyrolysis, there is a generally accepted reaction scheme. First, polypropylene melts and depolymerizes via random chain scission producing radical intermediates. The radical intermediates react to form primary products, represented by the solid blue pathways. The primary products can then undergo further reactions (e.g., interconversion and Diels-Alder), represented by the dashed red pathways, forming secondary and higher products.^{19,20,25,71}

While there is some agreement on the general structure of the polypropylene pyrolysis reaction network, there is little agreement on the underlying kinetics of the process, with significant variation in reported product distributions and reaction kinetic parameters. For example, reported lumped activation energies vary between 21 and 393 kJ mol⁻¹, and reported pre-exponential factors differ by up to 27 orders of magnitude.^{24,62,72} The variation in the available data is further demonstrated by **Figure 2**, which presents 215 reported apparent activation energies and pre-exponential factors for PP pyrolysis from 50





Figure 2. Literature-reported lumped polypropylene pyrolysis kinetics. (A) Distribution of reported activation energies. (B) Distribution of reported pre-exponential factors. (C) Compensation plot of pre-exponential factor (left-axis) and activation entropy (right-axis) versus activation energy, with associated experimental parameters provided for each data point.

literature sources; complete details on the data presented in this figure are available in the Supporting Information. These discrepancies can be attributed to variations in experimental conditions, such as heating and cooling rates, design.62,73-79 residence time, and reactor Additionally, heat and mass transfer limitations are often present due to large sample length scales (e.g., pellets and packed powders) which produce a distribution of reaction kinetics in the pyrolyzing mass.^{18,73,77,78,80-84} The influence of operational conditions on the kinetic parameters indicates that previous studies have reported apparent kinetics with transport artifacts rather than intrinsic reaction kinetics.

Intrinsic reaction kinetics will be essential for developing a fundamental understanding of polypropylene pyrolysis and for the design and optimization of scalable pyrolysis reactors.⁸⁵ To study the intrinsic reaction kinetics of polypropylene pyrolysis, a reactor system absent heat and mass transport limitations is required that also can measure time-resolved evolution of the polymer and its pyrolysis products. To this end, the Pulse Heated Analysis of Solid Reactions (PHASR) reactor was redesigned for polyolefin pyrolysis and validated with low-density polyethylene.⁸⁶ In this work, the use of the PHASR reactor with polypropylene was validated and isothermal, reaction-controlled operation was demonstrated, yielding polypropylene pyrolysis evolution curves between 525 °C and 625 °C that are then compared to literature data. Lastly, solid residues formed during polypropylene pyrolysis were analyzed to understand the competing pathways to volatile and non-volatile polypropylene products.

2.0 Methods. The PHASR reactor was originally developed by Krumm et al. for cellulose pyrolysis and has been redesigned to meet the challenges of polyolefin pyrolysis.^{86,87} The redesigned PHASR reactor is capable of measuring the intrinsic kinetics of polyolefin pyrolysis on the millisecond scale at temperatures up to 700 °C. The primary features of the PHASR reactor redesign include a new cylindrical reactor housing, a flange seal with a



Figure 3. Thin Film Polypropylene Samples. (A) Photograph of a 3 mm diameter thin film deposited on a sample plate. (B) Profilometry of a thin film showing an average thickness of ~13.5 μ m. (C) Uniformity of sample weights compared to sample thickness, as measured by a microgram-resolution balance. (D) Consistency of virgin polypropylene (PP) pellet and PP thin film TGA profiles, indicating no change to the thermal properties of the sample. (E) Cartoon depicting the reaction progress of a PP thin film.

copper O-ring, a modified heat exchanger, and beryllium copper contact brushes. As a result of these changes, the reactor body can be held at higher temperatures to prevent polyolefin pyrolysate condensation within the reactor. In addition, these changes have resulted in faster, more consistent heating and cooling times (≤ 20 ms and ≤ 180 ms, respectively) as well as more stable reaction temperatures. Full details of the reactor modifications and validation of reactor operating conditions are provided in previous work.⁸⁶

A full description of the PHASR method has previously been provided,⁸⁶ and a summary of PHASR operation is presented here. To perform PHASR experiments, thin film PP samples (15 µm thick, 3 mm diameter) are deposited onto passivated carbon steel sample plates and placed into the reaction chamber. When the reactor is closed, electrical feedthroughs contact the sample plate via beryllium copper contact brushes, allowing for a high current electrical pulse to be delivered to the sample plate. This electrical pulse resistively heats the sample plate to the pre-selected reaction temperature (\leq 700 °C) for the set reaction time (20 ms to 2.0 s); a cartoon depiction of reaction progress is shown in Figure 3e. During an electrical pulse, a 1000 Hz optical pyrometer monitors the

surface temperature of the sample and ensures precise temperature control through a PID feedback loop. Before performing a reaction, the reactor housing is heated to 300 °C to prevent pyrolysate condensation. A silicon heat transfer fluid (DOW Syltherm 800) continuously flows through a goldplated heat exchanger to rapidly cool the sample and quench the reaction. To prevent electrical shorting, an aluminum nitride ceramic sheet (0.010" thick) is present between the sample plate and the heat exchanger. Helium continually sweeps the reaction chamber (~360 ml/min), providing an inert atmosphere and carrying all volatile products to an in-line gas chromatograph with a Polyarc[®] & flame ionization detector (GC-PA-FID) for analysis. In this system, before analysis in the FID, all organic compounds are catalytically converted to methane in a Polyarc[®], eliminating response factor changes due to different compounds and calibrations and improving analysis accuracy.88

To operate under reaction-controlled conditions, thin film samples were used in PHASR experiments. To prepare thin film PP samples, PP pellets (provided by the ExxonMobil Technology and Engineering Company, MW ~263,000 g/mol by light scattering) were pressed in a Specac Mini-Film Maker at 175 °C with 0.5 tons of force for 30



Figure 4. Polypropylene transport properties. (**A**) Pyrolysis map comparing the two Pyrolysis Numbers and the Biot Number provides an order of magnitude estimation for the length scales and temperatures at which reaction-controlled pyrolysis is possible. (**B**) Mass transport map comparing the second Damköhler number to the characteristic length scale (i.e., thickness) of a polypropylene sample, providing an order of magnitude estimate for the length scale leading to the onset of transport limitations. Further information on these analyses is provided in the Supporting Information.

seconds. This produced thin film discs (~1.5 cm diameter) with thicknesses of 15 to 500 µm, from which individual 3.0 mm diameter PP samples were cut using a Harris Uni-Core micro-punch. 15 µm thick samples were primarily used for this work, and the thicknesses of the produced samples were verified using a KLA Tencor P-16 Surface Profiler, demonstrating that the average sample height is within ~1 µm of the desired 15 µm thickness (Figure 3b). Samples thinner than 15 µm were prepared by pressing the 15 µm samples in the Mini-Film Maker again (150 °C, 1 ton force, 30 s), resulting in films with a thickness of ~6 µm and a diameter of ~4 mm; example surface profilometry results are provided in the Supporting Information. For this work, initial sample weights were measured using a microgram-resolution balance (Metter Toledo XPR2U). The samples were produced with a high level of control, as shown by the consistency of sample weight versus sample thickness (Figure 3c). After weighing, the samples were deposited onto carbon steel sample plates at 165 °C until the samples lightly darkened on the surface (Figure 3a); this temperature was selected to prevent sample spreading during deposition. Prior to depositing the PP thin films, the sample plates were wiped with isopropanol and heated with a butane torch until the metal turned blue, thereby

cleaning and passivating the surface. To ensure the sample preparation process did not influence the degradation properties of PP, the original pellets and pressed thin film samples of PP were pyrolyzed in a TGA (He atmosphere at 100 ml min⁻¹, 30 to 1000 °C, 10 °C min⁻¹ ramp rate). The weight loss and derivative curves for both the original PP pellets and pressed PP thin films are overlaid in **Figure 3d**. The consistency between the original PP and the pressed PP indicates that no change to the degradation properties was caused by the sample preparation process.

In this work, samples were pyrolyzed over a range of temperatures (525, 550, 575, 600, and 625 °C) for reaction times between 20 and 2000 ms. The yield of light products ($<C_{20}$) was quantified via the in-line GC-PA-FID (GC-detectable yield). After pyrolysis, the amount of any remaining unreacted sample or residue on the plates was quantified with the XPR2U balance (MB). First, the excess area on the sample plates was cut off (to reduce the weight and improve weighing accuracy) and the plates were weighed. Then, the cut plates were soaked in 1,2,4-Trichlorobenzene (TCB, 99%, Alfa Aesar) at 150 °C for ~15 min to remove the remaining sample and residue. After drying in air, the clean plates were weighed again. The difference in the weights determined the weight of the





Figure 5. Simulated transient temperature profiles in polypropylene films. (A) 15 μ m thick sample with a target temperature of 500 °C. (B) 100 μ m thick sample with a target temperature of 500 °C. (C) Final temperatures for samples of different thicknesses after 100 ms and a target temperature of 500 °C.

remaining unreacted sample. Using the initial sample weights and the weight of remaining unreacted sample, the total yield of volatile products by mass was obtained (MB-detectable yield).

A second, Visual PHASR system was developed which enables in situ observation of reacting polypropylene pyrolysis samples via highspeed photography.⁸⁶ In this work, samples were pyrolyzed over a range of temperatures (500, 550, 600, 650, and 700 °C) for reaction times of 2000 ms. Within the Visual PHASR reactor, samples were pyrolyzed in the same manner as with PHASR, via controlled high current electrical pulses. For this system, the top assembly of a PHASR reactor was inverted and a 316 stainless steel riser containing clear polycarbonate side windows and a clear polycarbonate cover sealed the system, allowing for a helium atmosphere as well as observation of the samples with the high-speed camera. The Visual PHASR reactor is described in full detail in previous work.86

3.0 Results and Discussion.

3.1 Verification of isothermal, reaction-controlled operation. To obtain intrinsic reaction kinetics, it was necessary to operate under reaction-controlled conditions. To determine the limiting parameters (reaction temperature and sample length scale) of the regime in which PP pyrolysis occurs absent transport limitations, dimensional analyses of the heat and mass transfer properties of the reacting PP system were performed. To analyze the heat transport characteristics of the PP system, the pyrolysis numbers $(Py^{I} \text{ and } Py^{II})$ were plotted against the Biot number (Bi) producing a pyrolysis map, Figure 4a. Pv^{I} and Pv^{II} relate the timescale of reaction to the timescales of conduction and convection, respectively, and the timescales of conduction and convection are compared by Bi. The resulting order of magnitude estimate of this analysis indicates that it is possible to measure the intrinsic reaction kinetics of PP pyrolysis at temperatures up to ~650 °C with sample length scales of order 10 µm or less, as described by the top-left section highlighted in Figure 4a, wherein heat transport (conduction and convection) occurs



faster than reaction. An analogous dimensional analysis was performed for mass transfer within a PP sample. Here, the second Damköhler number (Da_{II}) , the ratio of the rate of reaction to the rate of diffusion. was plotted mass against the characteristic length scale of PP (i.e., the sample thickness), as shown in Figure 4b. This analysis shows that PP samples with length scales of order 100 µm or thinner are reaction controlled, with diffusion occurring orders of magnitude faster than Definitions, selected parameters, reaction. assumptions, and associated calculations for all dimensional quantities are provided in the Supporting Information.

The dimensional analyses indicate that heat transfer limitations are more likely to arise than mass transfer limitations, demonstrated by the difference in the order of magnitude estimates for the maximum allowable sample length scale to maintain reaction-controlled conditions (10 µm vs 100 µm). Heat transport was further analyzed with a 1-D simulation in MATLAB. The simulated system, a PP film atop a steel sample plate with a He atmosphere, includes conduction at the film/plate interface, conduction through the film. reaction kinetics throughout the film, and convection at the film/atmosphere interface. All selected parameters and complete simulation details are provided in the Supporting Information. Figures 5a and 5b show the same transient temperature profiles for simulated PP films with thicknesses of 15 µm and 100 µm, respectively, being heated to a target reaction temperature of 500 °C. The 15 µm film heated rapidly and uniformly, reaching ~300 °C in the first 10 ms and approximately reaching the 500 °C setpoint after just 30 ms of heating. Conversely, the 100 µm film was shown to heat in a non-ideal fashion, with large temperature gradients observed at all times; the maximum film temperature was more than 100 °C below the target temperature after 100 ms of heating. The effect of sample thickness on heat transport is further demonstrated by Figure 5c, which plots the simulated temperature profiles of films with thicknesses ranging between 15 µm and 500 µm after 100 ms. These data show that even a small increase in the film thickness from 15 µm to 25 µm results in a lower film temperature at 100 ms; however, the profile is still highly uniform. At all greater thicknesses, there is a notable decrease in film temperatures and increasing non-uniformity



Figure 6. Experimental verification of the transition between reaction-controlled and transport-controlled operation. Product yields detected by gas chromatography (GC, red squares) and microgramresolution balance (MB, navy circles) plotted as a function of sample film thickness for pyrolysis reaction performed at 625 °C for 60 ms. Pyrolysis reactions performed with samples thinner than 15 µm are reactioncontrolled (green region) and transport-controlled (gray region) when performed with samples thicker than 15 μm.

in the thermal profiles. The results of these simulations further demonstrate the necessity for fine control over the length scales of the PP samples to achieve isothermal, reaction-controlled pyrolysis conditions.

The dimensional analyses and heat transport simulations are reliant upon parameters found in the literature that are non-specific to the material and reactor used for this work, and as such can only provide an order of magnitude estimate for the maximum film thickness and reaction temperatures that define the isothermal, reactioncontrolled regime. Given this limitation, the transport-controlled transition between and reaction-controlled polypropylene pyrolysis regimes was experimentally verified. Here, a series of PP films of thicknesses ranging between 6 µm and 50 µm were prepared and pyrolyzed in the PHASR reactor at 625 °C for 60 ms. A minimum of three reactions were performed for each thickness and the product yields, measured by both gas chromatography (GC) and microgram-resolution balance (MB), are plotted in Figure 6. For the 15, 25, and 50 µm thick samples, a continuous decrease in the GC- and MB-detectable yields was observed



with increasing thickness, demonstrating the experiments are transport limited at thicknesses greater than 15 μ m with the limitations increasing

as a function of thickness. In contrast, the observed product yields were equal for PP samples with thicknesses of 6 and 15 $\mu m,$ indicating reaction-



Figure 7. Visual PHASR – Side View. Individual frames of high-speed video (1000 fps) of polypropylene thin films pyrolyzed at 500–700 °C for 2.0 s in the Visual PHASR reactor.



Figure 8. Visual PHASR – Top View. Individual frames of high-speed video (1000 fps) of polypropylene thin films pyrolyzed at 500–700 °C for 2.0 s in the Visual PHASR reactor.

controlled conditions absent heat and mass transfer limitations at thicknesses less than or equal to 15 μ m. Through the combined theoretical and experimental results, it is clear that PP pyrolysis via the PHASR method results in isothermal, reactioncontrolled conditions capable of quantifying intrinsic reaction kinetics.

3.2 Visual PHASR. Pyrolysis of PP films was observed with high-speed photography (1000 fps) at 500, 550, 600, 650, and 700 °C for two seconds within the Visual PHASR reactor. In all experimental trials, 15 µm thick, 3 mm diameter PP samples were used. Individual frames from the high-speed video (at 0, 0.4, 0.8, 1.2, 1.6, and 2.0 s) are shown in Figures 7 and 8, and the original videos are available in both real-time and slow motion in the Supporting Information. In all cases, the PP thin films are observed to react in a uniform manner, further establishing that the PHASR method enables isothermal, reaction-controlled conditions. Additionally, these videos enable a qualitative assessment of the rate and extent of reaction. At 500 °C, the apparent extent and rate of reaction are low, with little visual change to the sample occurring and large amounts of residue remaining on the plate after two seconds. At 550 °C and 600 °C, notable changes occurred to the samples as the reactions proceeded at a greater rate

with less residue remaining after two seconds. At the highest reaction temperatures of 650 and 700 °C, the reactions occurred rapidly, reaching completion in less than 0.5 seconds, with the solid films rapidly forming a molten phase and eventually into fully evolved vapors and gases with no observable residue remaining on the plates.

High speed photography of reacting PP films also revealed complex multi-phase behavior including the formation of bubbles, generation of aerosols, and a potential Leidenfrost effect of the polypropylene droplet on the hot plate, as shown in additional frames of video of a PP film reacted at 600 °C in Figure 9. At all temperatures, bubbles were observed to form with the evolution of volatile species in the melt phase, with the degree of bubble formation greatly increasing as a function of temperature. At 500 and 550 °C, small pockets of bubbles formed that remained independent, while bubbles formed throughout the reacting films and rapidly coalesced as the reaction proceeded at temperatures greater than or equal to 600 °C. The presence of bubbles agrees with prior descriptions and observations of PP pyrolysis in the literature.^{89,90} It is known that the presence and subsequent bursting of bubbles may lead to aerosol generation.⁹¹ The majority of aerosols formed, either by bubble film fragmentation or jet ejections.

15 ms	25 ms	135 ms	386 ms
428 ms	429 ms	430 ms	432 ms
565 ms	584 ms	585 ms	598 ms
650 ms	731 ms	812 ms	882 ms

Figure 9. Visual PHASR – Observed Reaction Phenomena. Individual frames of high-speed video (1000 fps) of a polypropylene thin film pyrolyzed at 600 °C for 2.0 s in the Visual PHASR reactor, depicting bubble formation, sample movement due to a potential Leidenfrost effect, and aerosol ejection.





Figure 10. Polypropylene pyrolysis yield versus time. (A) Yield of light products ($<C_{20}$) measured by gas chromatography (GC). (B) Yield of all volatile products measured by microgram-resolution balance (MB).

likely existed at a size below the observable limit afforded by video resolution; however, jet ejection of a large aerosol (> $2 \mu m$) was observed at 600 °C. This jet ejection event is shown in Figure 9 in the frames for reaction times spanning 428 to 432 ms. At 550 and 600 °C, the bubbles that formed moved along the surface of the sample plate. As shown in Figure 7, the small pockets of bubbles formed at 550 °C spread from the center of the sample plate in multiple directions. At 600 °C, as shown in both Figures 7 and 9, a primary cluster of bubbles formed which moved toward the back-right side of the plate. At 650 and 700 °C, significant sample movement was not observed, which may be due to the high rate of reaction at these temperatures. The sample movement may be evidence of a Leidenfrost effect; however, the movement may have also been induced by the helium atmosphere sweeping through the Visual PHASR reactor.

3.3 Intrinsic Polypropylene Reaction Kinetics. To measure the intrinsic reaction kinetics of PP pyrolysis, PP pyrolysis reactions were performed via the PHASR method at 525, 550, 575, 600, and 625 °C for reaction times ranging between 20 ms and 2.0 s. A minimum of three reaction trials were conducted for each unique time and temperature condition, and all yield data from these reactions are shown in **Figure 10**. Volatile products up to C_{20} were quantified as the GC-detectable product yield (Figure 10a), and the total yield of volatile products by mass was quantified as the MBdetectable product yield (Figure 10b). In both the GC- and MB-detectable product yields, it was observed that a maximum was reached at all temperatures between 140 ms (625 °C) to 300 ms (525 °C). Further increases in the product yields were not observed in the additional reaction period up to 2.0 s. Furthermore, the measured product yields agreed well with the qualitatively observed

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Figure 11. Kinetic analysis of polypropylene pyrolysis yield versus time. (**A**) Yield of light products ($<C_{20}$) measured by gas chromatography (GC) (points) with first-order model fits (solid lines). (**B**) Yield of all volatile products measured by microgram-resolution balance (MB) (points) with first-order model fits (solid lines). (**C**) Arrhenius plot of GC-detected (red circles) and MB-detected (navy squares) model fits, with linear regression analysis for determination of kinetic parameters. Complete details of model fitting are provided in the Supporting Information.

extents of reaction in the Visual PHASR reactor. In the Visual PHASR experiments at 500 and 550 °C, large amounts of residue were observed to remain on the plate, while at ≥ 600 °C, little to no residue remains after 2.0 s of reaction. The maximum MBdetectable product yields increase from ~15% at 525 °C to ~95% at 625 °C. Even in cases where no visible residue remains, typical of reactions at 625 °C for reactions times >140 ms, the 1,2,4-Trichlorobenzene cleaning process revealed a small amount of residue was still present.

To describe the kinetics of the primary reaction mechanism of PP pyrolysis outlined in **Figure 1**, a first-order consumption model (**Equation 1**) was fit to the experimental data. The kinetic parameters were fit using the short reaction time data, which encompasses the observed initial period of reactivity. In Figures 11a and 11b, the model fits are plotted as solid lines, and the 95% confidence intervals are plotted as dashed lines, overlaying the short reaction time yield data up to 300 ms. In Figure 11c, the Arrhenius plot is provided for both models, and the values of the kinetic parameters are listed in Table 1. Given the MB-detectable product yields represent all products that volatilize at a given reaction temperature, the MB-detectable model parameters better describe the overall intrinsic reaction kinetics of PP while the GC-detectable pyrolysis, model parameters describe the intrinsic kinetics for the production of light species up to C_{20} .

$$Y(t) = 1 - e^{-kt}$$
 (1)

Table 1. Intrinsic	Kinetic Model Pa	arameters
	E _a [kJ mol ⁻¹]	$\ln(k_0)$ [ln(s ⁻¹)

	E _a [kJ mol ⁻¹]	$\ln(k_0) \left[\ln(s^{-1})\right]$
GC-detected	171.1 ± 14.6	24.6 ± 2.4
MB-detected	242.0 ± 2.9	35.5 ± 0.6

3.4 Comparison of measured intrinsic reaction kinetics to literature data. As shown in Figure 2, a vast range exists in the literature for the reported kinetics of polypropylene pyrolysis, attributed to the measurement of apparent kinetics unique to a given experimental system rather than the intrinsic kinetics of the chemistry itself. The data presented in Figures 2a (reported apparent activation energies) and **2b** (reported pre-exponential factors) have been plotted together in Figure 2c as a compensation plot. In addition, the pre-exponential factors have been converted to activation entropy $(\Delta S^{\ddagger},$ Figure 2c right-axis) using Equation 2. In **Equation 2**, e is the natural logarithm base, k_h is the Boltzmann constant, h is the Planck constant, Tis the absolute temperature, and R is the universal gas constant.⁹² The line of best fit for ΔS^{\ddagger} versus E_{a} (black line) provides compensation, which was found to be 748 ± 36 K. Figure 2c also contains additional information on the sample sizes (symbol outlines), maximum reaction temperatures (symbol fill colors), and reactor types (symbol shapes) associated with the kinetic data. The literature data in this analysis are tabulated in the Supporting Information. The linear relationship between $\ln k_0$ and E_a observed in the compensation plot is an apparent compensation effect^{93,94} that further indicates that the literature-reported kinetics of polypropylene pyrolysis are representative of apparent rather than intrinsic kinetics. The kinetic parameters measured in this work, Table 1, are intrinsic to PP pyrolysis and are within the range of the previously reported parameters, aligning with the centers of the distributions conveyed in Figure 2, particularly the overall intrinsic kinetic parameters represented by the MB-detected model.

$$k_0 = \frac{ek_b T}{h} e^{\frac{\Delta S^{\ddagger}}{R}}$$
(2)

A mechanistic kinetic model to describe polypropylene pyrolysis and calculate estimates for the apparent activation energy was also derived. The radical reaction model was based upon the Rice-Herzfeld mechanism, commonly used to describe hydrocarbon chain decomposition and polyolefin pyrolysis.^{64,95–100} The model simply describes PP pyrolysis as a general radical reaction system in terms of initiation, propagation, and termination. Full details of the model derivation are provided in the Supporting Information and the derived rate expression is described by **Equation 3**. Here, k_i , k_H , k_β , and k_t are the rate constants for initiation, propagation (via hydrogen abstraction and β -scission), and termination, respectively. Species *A* represents the reacting PP.

$$r_{A} = \frac{d[A]}{dt} = k_{H} \left(\frac{k_{i}}{k_{t}}\right)^{1/2} \left(\frac{[A]^{3/2}}{1 + \frac{k_{H}}{k_{\beta}}[A]}\right)$$
(3)

Values were calculated for the elementary steps of the Rice-Herzfeld mechanism via DFT following a previously described method and utilized in combination with the derived rate expression to calculate apparent activation energies for PP pyrolysis.¹⁰¹ The DFT values were calculated for initiation via alkane C-C bond cleavage (~360 kJ mol⁻¹), propagation via β scission (~120 kJ mol⁻¹), propagation via hydrogen abstraction (~48 kJ mol⁻¹), and termination via radical recombination was assumed to have no energic cost.¹⁰¹ Three different termination mechanisms are considered for this model, R_1R_1 , R_2R_2 , and R_1R_2 , and the apparent activation energy of the system is dependent upon which of these mechanisms is dominant. The DFT activation energies were used to calculate the activation energies for R_1R_1 -, R_2R_2 -, and R_1R_2 -dominant termination, resulting in activation energies of 228, 300, and 264 kJ mol⁻¹, respectively. The calculated values are consistent with both the intrinsic kinetic model parameters experimentally obtained via the PHASR method and with the range of literaturereported parameters. Additional details on the use of the DFT-calculated values with the derived rate expression are provided in the Supporting Information.

3.5 Residue Analysis. The formation of residue product was observed at all reaction conditions other than 625 °C for reaction times exceeding 100 ms. Residue and char from polypropylene pyrolysis has been previously reported; however, there is little consistency in the definitions of the solids and





Figure 12. Analysis of solid residues. (**A**) Raman spectroscopy of polypropylene (PP) samples reacted at 525 °C for 20–2000 ms, with comparison to unreacted PP (Full spectra are provided in the Supporting Information). (**B**) Advanced attenuated total reflectance infrared (ATR-IR) corrected spectroscopy of PP samples reacted at 525 °C for 20–2000 ms, with comparison to unreacted PP (Full spectra are provided in the Supporting Information). (**C**) Microscope photograph of a PP sample reacted for 20 ms at 575 °C. (**D**) Microscope photograph of a PP sample reacted for 20 ms at 575 °C. (**F**) Microscope photograph of a PP sample reacted for 500 ms at 575 °C.

varying extent of formation.^{52,71,102-107} Given the consistent nature of residue formation in our experiments of Figure 10, the resulting solid residues from polypropylene pyrolysis were characterized. Char was analyzed by multiple methods including microscopy, ¹³C solid-state NMR, Raman spectroscopy, and attenuated total reflectance infrared (ATR-IR) spectroscopy. Other techniques, such as gel permeation chromatography (GPC), were not utilized due to low residue masses. The PP thin films used in the PHASR method to achieve isothermal, reaction-controlled conditions were $70 \pm 10 \,\mu g$ and yield residues of about 10 μg . Analytical capabilities were further limited by the need to remove the polypropylene pyrolysis residues from the experimental sample plate with solvent. Removal of residues from the sample plates with mechanical means (i.e., scraping, tweezers, etc.) was found to be ineffective, with only the use of excess 1.2.4-trichlorobenzene at 150 °C proving to consistently and reliably remove the

residues. Consequently, the dissolved residues were dilute (~1 μ g ml⁻¹) and not suitable for techniques like GPC which require sample concentrations of ~1 mg ml⁻¹. An analysis of the product residue with ¹³C solid-state NMR was made possible by combining multiple 250 μ m thick samples to meet the effective sample mass threshold of ~20 mg; however, commensurate with the results of **Figure 6**, these thick films were observed to have a low degree of conversion when pyrolyzed for 2.0 s due to the impact of transport limitations and the NMR spectrum was unchanged as compared to virgin PP. Additional details on the NMR analysis are provided in the Supporting Information.

A simple visual analysis of the formed residues was performed through examination with an optical microscope. Photographs of the samples reacted at 575 °C for 20, 100, 220, and 500 ms taken through the eye-piece of the microscope are shown in **Figure 12c-f**. The sample reacted for 20 ms (**Figure 12c**) is primarily clear, with indications of



Figure 13. Secondary polypropylene reaction kinetics. (**A**) Cumulative gas chromatography (GC) detected yields of polypropylene (PP) samples pyrolyzed for 31 successive 2.0 s pulses (total reaction time of 62.0 seconds) at 500 °C (**B**) Cumulative GC detected yields of PP samples pyrolyzed for 13 successive 2.0 s pulses (total reaction time of 26.0 seconds) at 525 °C

bubbling due to gas and vapor product volatilization, and it has retained its original circular shape and ~3.0 mm size. Similarly, the sample reacted for 100 ms (**Figure 12d**) has mostly retained its original size and shape; however, the sample is notably darker, indicating the potential formation of char-like material. The sample reacted for 220 ms (**Figure 12e**) has evidence of sample spreading and movement, as previously observed in the Visual PHASR, as well as potential char-like material. The sample reacted for 500 ms (**Figure 12f**) has a small amount of thin, dark residue, that is again indicative of potential char-like material.

The product residues of samples reacted at 525 °C for 20 to 2000 ms, as well as unreacted PP, were further analyzed by Raman, ATR-IR, and advanced ATR-IR corrected spectroscopy. The notable results of these analyses are depicted in Figures 12a-b. In the Raman spectra (Figure 12a), a new peak was observed at ~1648 cm⁻¹ for samples reacted at 525 °C for times ≥ 100 ms that was not observed in unreacted and virgin PP samples. This peak corresponds to a substituted alkene to C-C double bond.¹⁰⁸ In the advanced ATR-IR corrected spectra (Figure 12b), a new peak was observed at ~886 cm⁻¹ that was not present in the unreacted PP, which corresponds to a substituted alkene or aromatic C-H bonds.^{108,109} The results from both analyses are indicative of the formation of unsaturated species that may be precursors to or polyaromatic in nature. The formation of these new chemical structures that react slower than virgin polypropylene may explain the plateauing yields of

volatile products in short reaction times up to 2.0 s as depicted by **Figure 10**. Additional details on these analyses, including the full spectra, are available in the Supporting Information.

3.6 Secondary Polypropylene Pyrolysis Kinetics. Spectroscopic analysis of the solid residues produced at short reaction times of up to 2.0 s in the PHASR reactor revealed the formation of unsaturated species. The stability of these residues was tested to determine whether these changes to the original PP prohibit further reaction or generate a secondary kinetic regime wherein the material pyrolyzes at a reduced rate at times beyond the measurement of the PHASR reactor. Under standard operation, the PHASR reaction is limited to reaction times of 2.0 s for a single pulse. This is an inherent safety limit of the PHASR power supply controller, which is designed to deliver high current electrical pulses for times up to 2.0 s, that cannot be bypassed.⁸⁶ To probe reaction times longer than 2.0 s, we instead utilized multiple successive 2.0 s thermal pulses on individual samples.

When samples are reacted within the PHASR reactor, the sample plate undergoes intense stresses induced by the high current electrical pulses (~1.3 kA, 4V) and rapid thermal swings (heating from room temperature up to 500–700 °C in <20 ms and cooling back to room temperature <180 ms). These extreme conditions lead to embrittlement of the sample plates, with some plates failing during a single pulse. For these long reaction time experiments, the vast majority of the sample plates failed after only two to four

successive 2.0 s pulses (total reaction times of 4.0 to 8.0 s); however, three samples withstood 31 successive pulses at 500 °C (total reaction time of 62.0 s) and two samples withstood 13 successive pulses at 525 °C (total reaction time of 26.0 s). The lower reaction temperatures of 500 and 525 °C were chosen as they allow for slightly lower amperage currents to be used, ~1.2 kA.

The average cumulative GC-detectable product yields from these samples are plotted in **Figures 13a** and **13b**, with yield data from times shorter than 2.0s from prior experiments also included. At both 500 °C (**Figure 13a**) and 525 °C (**Figure 13b**), the GC-detectable yields achieved after 2.0 s were in agreement with the yield data in **Figure 10**, with average yields of ~7% and ~10%, respectively. In the multi-pulse experiments at both 500 °C and 525 °C, the yields were observed to consistently rise with each thermal pulse after the initial 2.0 s up to ~12% and ~13%, respectively, after which the plates failed.

The reactivity of the solid residues at reaction times longer than 2.0 s was significantly slower than the fast, millisecond reactivity observed in the initial ~0.3 s of PP pyrolysis, revealing the existence of a secondary kinetic regime. This secondary kinetic regime likely results from the desaturation of the original PP material, as detected by Raman and ATR-IR spectroscopy, as well as by the presence of char-like material observed in the microscope photographs (Figure 12). PP pyrolysis at 525 to 625 °C may be described by a two-stage lumped reaction system (Scheme 1). The first stage is characterized by rapid millisecond kinetics and the initial generation of gases and vapors, as well as solid pyrolysis residue. The second stage is characterized by the continued reaction of the solid residue to form additional gases and vapors, as well as solid, unreactive char on the second-to-minute timescale. The kinetics of the secondary kinetic regime will be the focus of future work.

4.0 Conclusions. The intrinsic reaction kinetics of polypropylene (PP) pyrolysis have been evaluated via the method of Pulse-Heated Analysis of Solid Reactions (PHASR) at temperatures spanning 525 to 625 °C for reaction times between 20 ms and 2.0 s. The PHASR method was validated theoretically and experimentally to react ~15 μ m thin films absent heat and mass transfer limitations. Direct



Scheme 1. Two-stage lumped reaction scheme for polypropylene pyrolysis at 525-625 °C. Polypropylene pyrolysis is described by a two-stage lumped reaction system characterized by rapid millisecond kinetics and initial generation of gases and vapors, as well as solid pyrolysis residue (stage 1) and the continued reaction of the solid residue to form additional gases and vapors, as well as solid, unreactive char on the second-to-minute timescale (stage 2).

observation of reaction PP films via high-speed photography elucidated reaction phenomena, including bubble formation, aerosol ejection, sample movement due to a potential Leidenfrost effect, and residue formation. A maximum plateau effect in the observed yields for reactions less than 2.0 seconds was observed at all reaction conditions other than 625 °C, where complete reaction was reached in ~100 ms. A lumped first-order consumption model was used to determine the overall reaction kinetics, representative of the microgram-resolution balance detectable yields, resulting in an activation energy of 242.0 ± 2.9 kJ mol⁻¹ and a pre-exponential factor of $35.5 \pm 0.6 \ln(s^{-1})$ ¹).The residues observed to form in the first 2.0 s of PP pyrolysis were shown to have a dark, char-like appearance, and the formation of unsaturated species was detected by Raman and ATR-IR spectroscopy. The stability of residues was explored at reaction times exceeding 2.0 s revealing the existence of a secondary kinetic regime in which the PP pyrolysis residue continues to react on the second-to-minute time scale. The kinetics of the slow, secondary kinetic regime will be the focus of future work.

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Supporting Information. The Supporting Information is available online.

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