

Temperature-Dependent Pyrolytic Product Evolution Profile for Polypropylene

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ABSTRACT: The composition of the pyrolysis products of plastics depends on disintegration of the macromolecule into variety of hydrocarbon fractions. In this work, a detailed gas chromatographic study of pyrolysis products of polypropylene (PP) between 200 and 600°C was carried out. The pyrograms have been analyzed in terms of amount of different products evolved at various pyrolysis temperatures. At low pyrolysis temperatures (200–300°C), the yield of lighter hydrocarbons (C5–C10) is low; it gradually increases until maximum decomposition temperature (446°C) and decreases thereafter. The following reaction

types were considered to explain the decomposition mechanism of PP: (a) main chain cleavage to form chain-terminus radicals; (b) intramolecular hydrogen transfer to generate internal radicals; (c) intermolecular hydrogen transfer to form both volatile products and radicals; and (d) β -scission to form both volatiles and terminally unsaturated polymer chains. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 2318–2325, 2011

Key words: poly(propylene) (PP); pyrolysis; thermogravimetric analysis (TGA); degradation

INTRODUCTION

Pyrolysis of plastics continues to draw the attention of researchers worldwide due to the tremendous potential of this voluminous waste to be converted into fuel, which otherwise would end up in landfills. The properties (energy content, viscosity, density, octane and cetane number, flash-point etc) of the pyrolysis-derived fuels from plastics are similar to conventional fuels.¹ Pyrolysis of plastics follows complex routes that cannot be described readily by one or more chemical reactions; usually only a comprehensive system of elementary reactions featuring fractional stoichiometric coefficients is used to describe these pathways.² On the other hand, knowledge of reaction pathway helps one to understand overall pyrolysis mechanism and aids in optimization of process parameters to obtain specific products. Moreover, the composition and structure of these reaction systems vary with details of molecular structure, such as chain irregularities, incorporation of initiators or catalysts, presence of additives etc. Product distribution study is of immense importance to have an insight of polymer degradation mechanism. Pyrolysis of polypropylene (PP) at different temperatures (350, 380, and 420°C) was examined by Kruse et al.²

and a mechanistic model using typical free radical reaction types including intermolecular hydrogen abstraction, intramolecular hydrogen transfer, mid/end-chain β -scission, radical addition/recombination, bond fission, and disproportionation was proposed to predict the formation of low molecular weight (C1–C15) products. Bockhorn et al.³ developed a kinetic model based on isothermal kinetics of polyethylene (PE) and PP and showed that rate equations formulated were consistent with measured rate coefficients. Peterson et al.⁴ used isoconversional method to calculate activation energies for polystyrene (PS), PP, and PE degradation as a function of extent of conversion and corresponding degradation mechanism was proposed. Detailed kinetic modeling of the thermal degradation of vinyl polymers was reported by Marongiu et al.⁵ with the help of a unifying approach. Ranzi et al.⁶ adopted a numerical approach to present a mechanistic kinetic model which described the radical chain pyrolysis reactions of PE and PP taking place in the liquid phase. Detailed kinetic models of PE, PP, PS, and mixtures of PS and poly (α -methylstyrene) (PMS) were investigated by Woo et al.⁷ and Richards et al.^{8–10} Stepwise pyrolysis of plastic mixtures was also reported in the literature, which confirms that different molecular structures of plastics bring about different reaction mechanisms of thermal decompositions.^{11,12} Walendziewski and Steinger¹³ reported thermal and catalytic degradation of PE between 370 and 450°C. In case of thermal degradation of PE, an increase in

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degradation temperature led to a modest increase of gas and liquid products with boiling point $< 360^{\circ}\text{C}$, combined with a sharp decrease in residue. Mastral et al.¹⁴ carried out pyrolysis of PE between 640 and 700°C with different residence times (0.8–2.6 s) in the reactor. They developed a model based on a radical mechanism that could predict the product distribution. Gas product distribution for pyrolysis of PE derived from random-scission hypothesis was proposed by Faravelli et al.¹⁵ Pyrolysis of a waste plastic mixture of high-density polyethylene (HDPE), low-density polyethylene (LDPE), PP, and PS was investigated at low (350°C) and high (400°C) temperatures to study the effect of lapse time of reaction and degradation temperature on characteristics of the liquid product.¹⁶ They observed that cumulative yield of the liquid product at 400°C increased sharply with lapse time of reaction compared to that at 350°C . Similarly, the following studies particularly aimed at elucidating the decomposition behavior of PP were also reported in the literature. Chan and Balke¹⁷ developed a comprehensive kinetic model to describe the change in molecular weight distribution of products during thermal degradation of PP. They also observed that with increase in residence time, molecular weights (both weight-average and number average) and polydispersity decreased. In another work, they studied the time-temperature superposition for degradation temperatures and reaction times from 225°C and 14 days to 375°C and 1 min.¹⁸ The extent of degradation was found to be similar for 2 min at 350°C , 12 h at 275°C , and 14 days at 250°C .

In one of our earlier works, we performed a pyrolysis-gas chromatographic study of LDPE.¹⁹ It was observed that LDPE degrades over a wide range of temperature (200 – 600°C) and produces a homologous series of hydrocarbons; a suitable reaction mechanism was also proposed for product evolution.

This work has been taken up with the motive to use a simple GC technique to understand the complex degradation behavior of PP, an important member of polyolefins family, over a wide range of temperature; to the best of our knowledge this kind of study has not been reported in the literature so far. The merit of this work lies in the fact that the simple analytical technique (such as the one used in this study) can be utilized for understanding the temperature dependency of product evolution as well as the underlying reaction pathways. In this study, we have carried out degradation of PP in a TGA and analyzed the pyrolyzate in a GC equipped with FID detector. We have monitored the product evolution (C5–C44) at six different temperatures from

200°C (where there is a negligible product formation) through 600°C (end of degradation). The GC results were used to study the product distribution and correlate the same with the decomposition mechanism of PP (including those available in the literature^{2,3}).

EXPERIMENTAL

Materials

PP used in this study was a homopolymer (PPHP, Trade Name: Koylene ADL AS030N). It was obtained from Indian Petrochemicals Corp. Limited, Vadodara, India. It has a melt flow index of 3.0, melting point of 175.6°C , heat of fusion of 62.38 J/g and a percentage crystallinity of 32.83.²⁰ Virgin PP was used in this study, to eliminate the effects of different additives and/or impurities present in waste PP; postconsumer plastics are also subjected to different thermal history during their processing, which may affect their thermal behavior.

Pyrolysis experiments

The polymer samples were shredded into very small pieces ($\sim 0.6\text{ mm}$) and placed into $150\text{-}\mu\text{L}$ platinum crucible and loaded on to the TGA weighing pan. The degradation experiments were carried out in a Thermo Gravimetric Analyzer (Make: Mettler Toledo, Model: TGA/SDTA 851^o) in an inert argon atmosphere (flow rate 40 – 50 mL/min). The sample was heated from ambient temperature at a heating rate of 10°C/min . Once the sample reached the desired degradation temperature (200 , 300 , 400 , 446 , 500 , or 600°C), 1 mL of the evolved sample (at atmospheric pressure) was collected and sent to GC for analysis.

GC calibration and product analysis

All GC experiments were performed using a Varian 3800 GC with an FID detector. An ultra low bleed Factor Four capillary column VF-200ms (Varian, Inc.) (30 m length, $0.25\text{ }\mu\text{m}$ film thickness, 0.25 mm ID) having 100% trifluoropropyl methyl siloxane phase was used for the separation. Carrier gas (N_2) flow rate of 1.5 mL/min was used and during the course of the run temperature was ramped from 30 to 300°C using a preset temperature program.

In an independent preliminary calibration procedure, two quantitative reference petroleum standards (ASTM D3710 and ASTM D5442) containing 27 known hydrocarbons (C5–C44) were injected into the GC. The analysis of these results yielded response

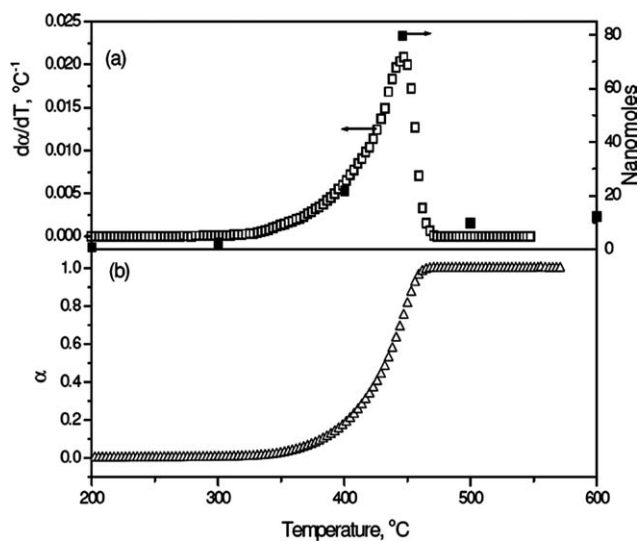


Figure 1 (a) Derivative thermogravimetric (DTG) curve of PP (on primary axis) and total moles evolved from pyrolysis of PP (on secondary axis); (b) Thermogravimetric (TG) curve of PP (heating rate: 10°C/min, Ar flow rate: 40 mL/min).

factors of the GC for the hydrocarbons present in the reference standards. Column oven program and other parameters were set so as to optimize separation between the different hydrocarbon species (C5-C44) in the standards used for calibration. This resulted in longer retention time for higher hydrocarbons from the column.

During the actual product analysis, 1 mL of sample evolved from the TGA at temperature of interest was drawn into a gas tight syringe and injected into the GC. Moles of the eluent hydrocarbons were calculated using the response factors obtained using the calibration procedure performed earlier.

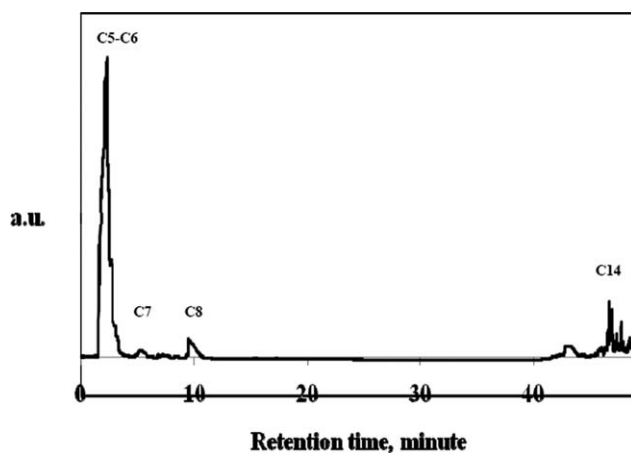


Figure 2 Partial chromatogram of PP pyrolyzate at T_{\max} (446°C) showing lighter hydrocarbons (C5-C15).

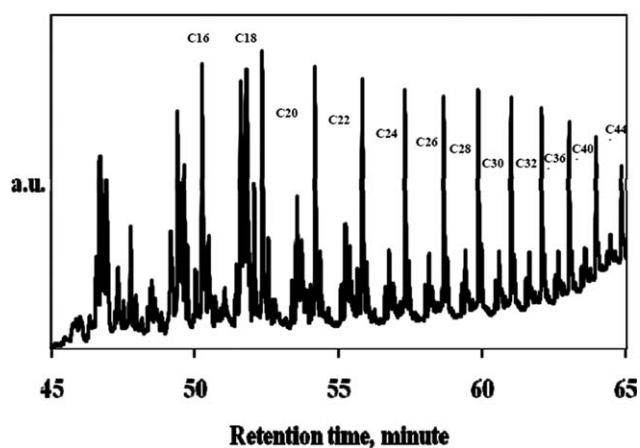


Figure 3 Partial chromatogram of PP pyrolyzate at T_{\max} (446°C) showing heavier hydrocarbons (C16-C44).

RESULTS AND DISCUSSION

Products analysis

A typical thermogravimetric (TG) curve for fractional mass conversion α is shown in Figure 1(a). The derivative thermogravimetric (DTG) curve for rate of degradation $\frac{d\alpha}{dT}$ of PP are shown in Figure 1(b). It is evident from this figure that maximum decomposition temperature (T_{\max}) for PP is around 446°C; earlier studies also support this observation.²¹ Figure 1(b) also depicts total moles of hydrocarbon products evolved (in 1 mL of vent gas from the TGA) as a function of degradation temperature; the evolved moles are calculated from GC analysis (to be discussed later). It can be seen that amount of evolved product closely follows the DTG curve. Pyrolysis product of PP contains aliphatic hydrocarbons with methyl branches as a major portion, indicative of the structure of the original polymer²²; the amount of straight aliphatics is usually lower. Figures 2 and 3 represent portions of the chromatogram of the pyrolysis products of PP evolved at T_{\max} . In

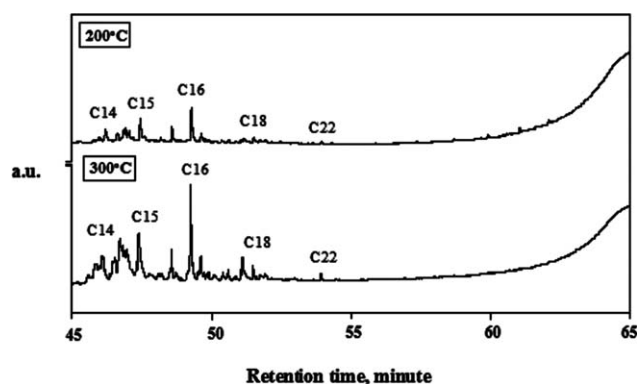


Figure 4 Partial chromatogram of PP at 200 and 300°C showing C14 and above hydrocarbons.

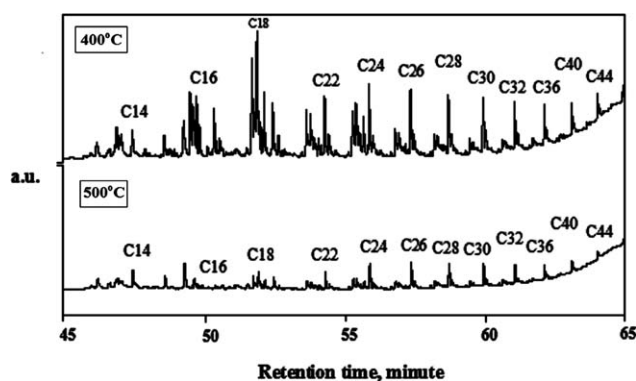


Figure 5 Partial chromatogram of PP at 400 and 500°C showing C14 and above hydrocarbons.

Figure 2, the first peak represents both C5-C6 en masse. Clearly, a wide range of hydrocarbons evolve from the pyrolysis. Figures 4 and 5 show partial chromatograms evolved at 200 and 300°C; and 400 and 500°C, respectively. A close look into these figures reveal changes in evolution pattern of the hydrocarbons in terms of carbon numbers, and thus indirectly indicates changes in molecular weight of the products as temperature changes. As can be seen in Figure 4, changes in molecular weight of the product is not very evident as we go from 200 to 300°C, only the amount evolved increases with temperature. But as temperature increases from 300 to 400°C, changes in molecular weight become quite significant (Fig. 5). The high molecular weight species beyond C24 evolve to a larger extent at 400°C, and beyond though their intensity decreases after 500°C. The amount of C5-C8 species is almost negligible at low temperature (being indistinct they are not shown in figure). But beyond 300°C, they evolve significantly (Fig. 2 shows C5-C7 species at T_{max}).

Figures 6 and 7 show the total moles and relative molar ratio of various hydrocarbons contained in the py-

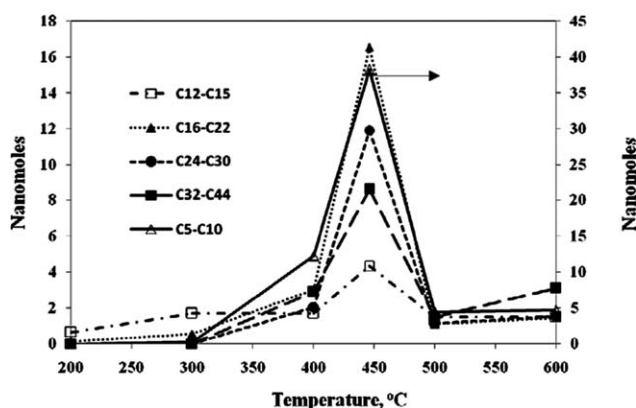


Figure 6 Temperature dependency of C5 to C44 evolution during pyrolysis of PP (C5-C10 on secondary axis, to the right; rest of all on primary axis).

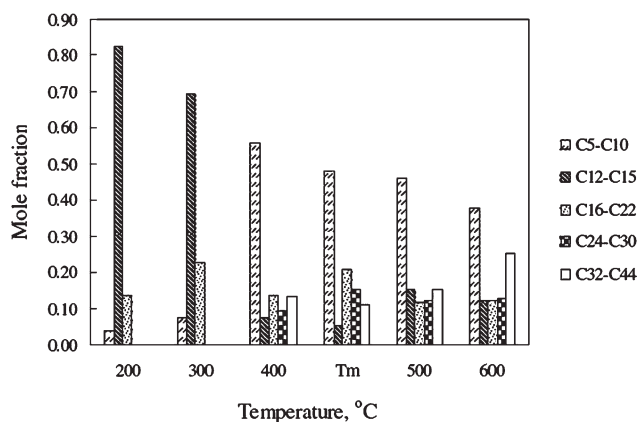


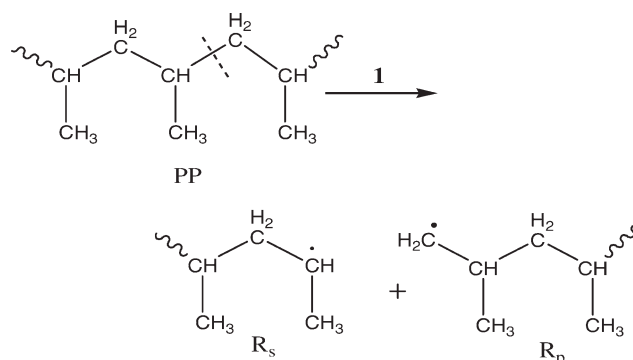
Figure 7 Fractional evolution of C5-C44 hydrocarbons.

rolysis product stream as a function of temperature. The change in composition of product with pyrolysis temperature is evident from this plot. Figure 6 clearly shows that hydrocarbon product yields depend strongly on decomposition temperature. At 200°C, where less energy is available for thermal cracking, some trace quantities of C12-C15 and C16-C22 hydrocarbons are detected (Fig. 6). This could be due to decomposition of weak bonds in the polymer molecule formed during polymerization process. Richards and Salter⁸⁻¹⁰ in their work evaluated thermal degradation of PS by using PMS as a radical producing agent and confirmed the contribution of these weak links in initiating the degradation at otherwise stable temperatures. Similar scenario may exist in case of PP as well. Weak links can exist in form of side chains, peroxy, carbonyl, hydroxyl group (formed in the process of radical polymerization of propylene), and atactic portions of macromolecular chain could induce the degradation at an earlier stage as these are most susceptible to thermal destruction.²³ However, we see a high proportion of C12-C15 in the product composition (Fig. 7), due to the absence of other fractions (C24 and above). At 300°C, yield of C12-C15 and C16-C22 slightly increases and a trace amount of C5-C10 hydrocarbons is detected (Fig. 6). Termination reactions play a vital role in characterizing product distribution. At low temperature of pyrolysis (200–300°C), radical recombination does not take place, which could be the reason behind the absence of heavy fragments in the pyrolyzate. From Figure 7, it is seen that as temperature increases from 200 to 300°C, relative yield of C5-C10 and C16-C22 increases. Figure 6 depicts that at 400°C, significant yield of C5-C10 is obtained due to increase in available thermal energy for cracking. As temperature proceeds, intensity of cracking reactions increase resulting in increased amount of lighter hydrocarbons. Yield of both C12-C15 and C16-C22 increases and some amounts of heavier hydrocarbons (C24-C30 and C32-C44) are also obtained at 400°C (Fig. 6). As we go from 300 to 400°C, there is an enormous increase in C5-C10 production, thereby increasing their concentration as compared to C12-C15

and C16-C22 fractions (Fig. 7). Production of heavy hydrocarbons (C24-C44) probably occurs due to the recombination reactions; at higher temperature, termination by radical recombination leads to the formation of heavy hydrocarbons. Since C5-C10 hydrocarbons are volatile enough to emerge from the molten pool, they escape into the gas phase without undergoing secondary reactions to a large extent. At 446°C, which is the maximum decomposition temperature, volatile product yield attains a maximum as cracking reactions become vigorous. Evolution of C5-C10 increases by more than hundredfold as compared with that at 200°C (Fig. 6). Yield of all other fractions increases roughly by 10-fold as compared with that at 400°C. At T_{\max} , relative yield of different hydrocarbons remains more or less the same, except that there are more of middle fractions (Fig. 7). Beyond T_{\max} , there is a decrease in the overall production of all the fractions. Abundance of heavier hydrocarbons indicates that termination by radical recombination is significant.

Mechanistic analysis

The reactivity of the system is governed by the overall radical pool; hence, the competition between initiation and termination reactions should be correctly accounted.²⁴ Thermal decomposition of PP initially proceeds essentially by random scission mechanism. The way in which a molecule fragments during pyrolysis and the identity of the fragments produced depend on the types of chemical bonds involved and the stability of the resulting smaller molecules.²² The proposed reaction pathway separately takes into account formation of alkanes, alkenes and diolefins and is considered to represent the product distribution. Initiation reactions can involve either C-C or C-H bond cleavage. Bond dissociation energy of C-C and C-H bonds are 347 kJ/mol and 413 kJ/mol, respectively. C-C bond dissociation is the more probable initiation step, since it is weaker of the two. PP undergoes random-scission reaction (1) giving rise to one primary radical (R_p) and one secondary radical (R_s).^{3,5,23}

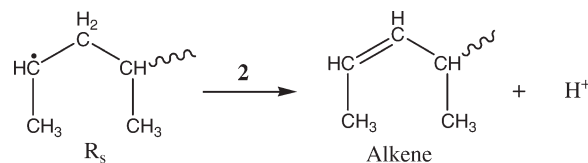


C-C bonds in PP are weaker than in PE due to the presence of tertiary carbon centers at every

second carbon atom in the chain backbone; hence, random scission starts at a lower temperature and thereby increasing the yield of product at 200°C for PP (Fig. 6) as compared with PE.¹⁹

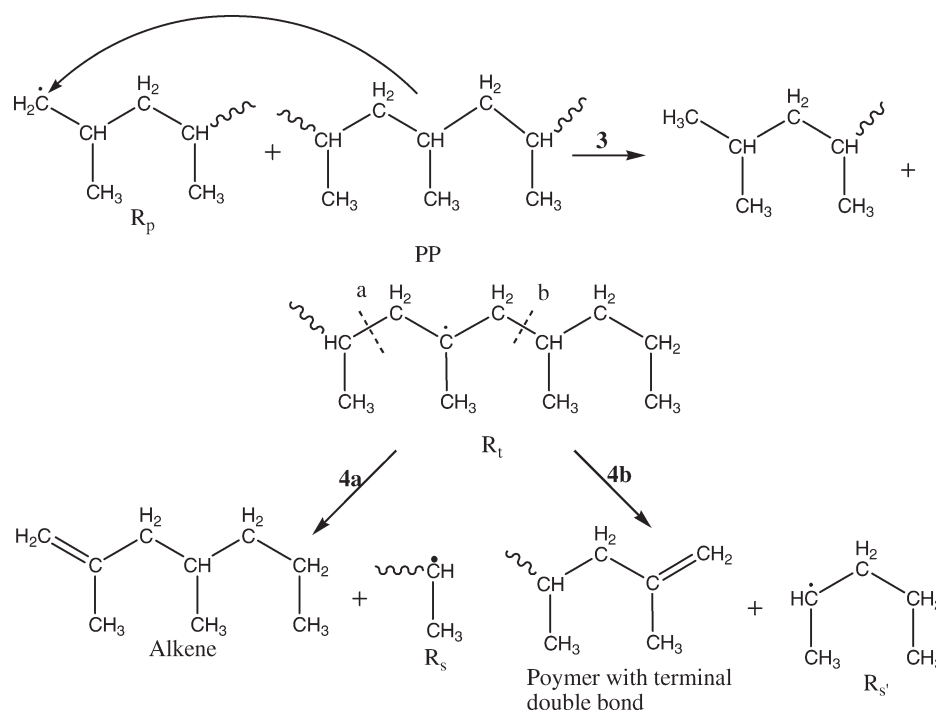
The different radicals thus formed from random scission of PP are capable of stabilizing themselves either by hydrogen abstraction, β -scission, or radical recombination, all of which form a stable molecule. The reaction that would be favored for stabilization depends on temperature; for example recombination reactions are favored at high temperatures and accordingly yield of higher hydrocarbons increases at high temperatures (Fig. 6).

At (200–300°C), where sufficient energy is not available for termination of radicals, abstraction is the preferred route for radical stabilization. Thus, R_s (having a low degree of polymerization) undergoes abstraction (reaction 2) to form an alkene. Reaction 2 justifies some trace quantities of C12 and higher hydrocarbons at these low temperatures. However as temperature increases, the increase in H^+ radicals somewhat slows down this reaction. Therefore, abstraction is probably not favored at high temperature.

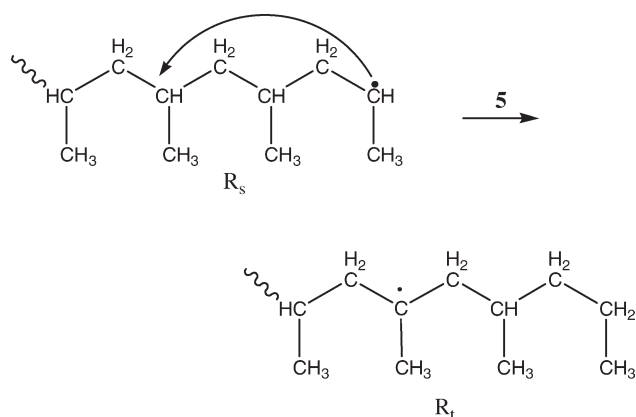


At high temperatures ($\geq 300^\circ\text{C}$), other reactions *viz.*, intermolecular and intramolecular H-transfer, β -scission, etc. become important. Since, R_p is less stable than either R_s or a tertiary radical (R_t), inter molecular hydrogen transfer occurs and R_p is converted to R_t (reaction 3). The H-atom attached to the tertiary C-atom is more reactive and can be easily detached (as compared with the secondary C-atom) and methyl group being small in size does not hinder migration of hydrogen atom.²⁴ Thus, the result of this reaction (3) is a methyl terminal group and a more stable R_t . The latter decomposes by β -scission (reaction 4) (either mid-chain or end-chain) giving rise to either an alkene, and a R_s , or polymer with terminal double bond, and a short secondary radical (R_s). Thus, at higher temperature intermolecular hydrogen transfer (reaction 3) takes place followed by β -scission (reactions 4a and 4b), which justifies the formation of more amount of lighter hydrocarbons beyond 300°C.

R_s (produced in reaction 1), on the other hand undergoes intramolecular hydrogen transfer (re-

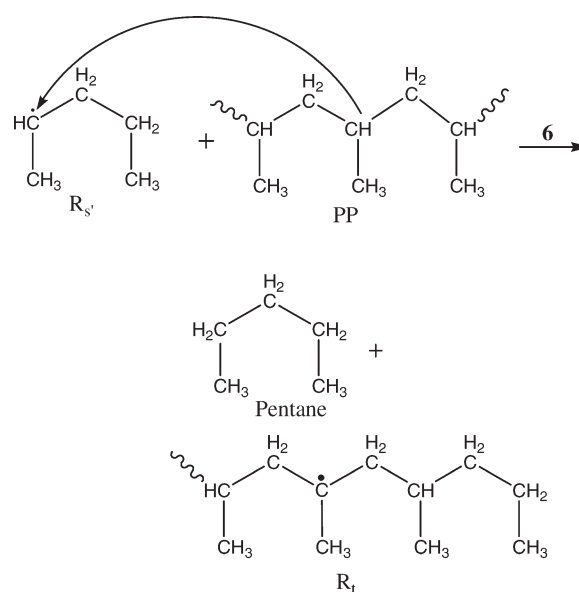


action 5) giving rise to a more stable R_t which decomposes by β -scission following route 4. Since R_s is regenerated, the chain reaction will continue and produce equal number of methyl and vinyl terminal groups in the fragments of gradually decreasing molecular mass.

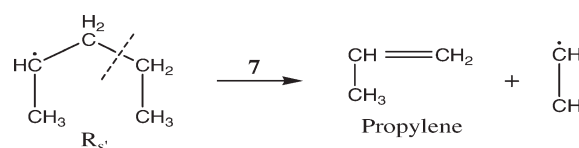


Intramolecular reactions such as the one shown in reaction 5 are crucial in the free radical mechanism of degradation of PP which justifies the wide range of hydrocarbons produced in the process.^{2,23,25,26} As suggested in the literature,^{1,2,27} 1,5-hydrogen transfer in R_s (reaction 5) is important in producing products such as dimers, trimers, tetramers, pentamers etc. In our study the preferential formation of some products such as C5, C6, C9, C12, C15, C18, C30, and C36 can be readily attributed to this mechanism. However, at these temperatures more of C5-C10, C12-C15 fractions are found in the product at 400–446°C, indicating more of one or two step intramolecular hydrogen transfer, rather than high order steps.

$R_{s'}$ (produced in reaction 4b) undergoes intermolecular hydrogen transfer (reaction 6) with a macromolecule of PP producing pentane and regenerating R_t .



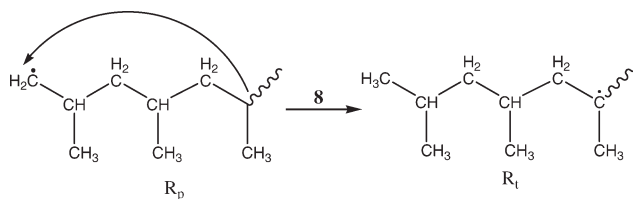
At 400–500°C, $R_{s'}$ can undergo β -scission (reaction 7) to produce propylene.



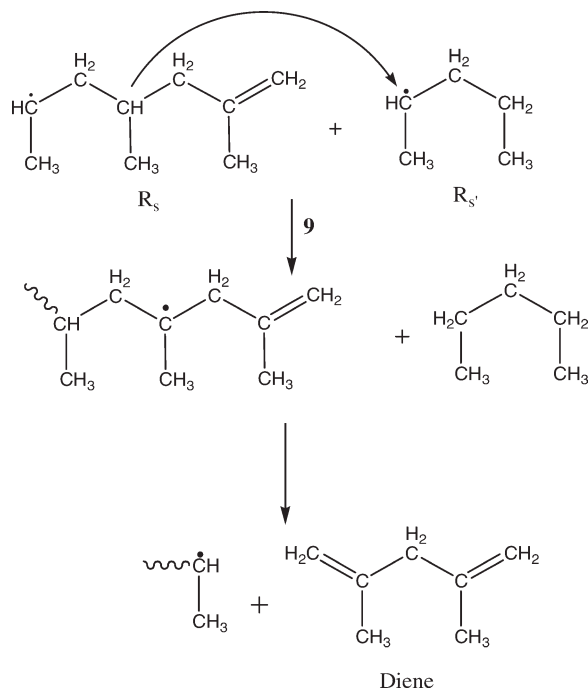
Similarly, R_p and R_s might also undergo unzipping or depolymerization to produce the propylene monomer. However, according to Lattimer,²⁵ unzipping to

monomer is not a favorable process below 400°C, when only traces of highly volatile (C1-C4) products are formed. Thus, both these reactions explain increase in yields of lower molecular weight hydrocarbons at higher temperatures (>400°C).

R_t may also result by the backbiting (1,6-hydrogen transfer) (reaction 8) of a primary macroradical, i.e.,



R_t , on intramolecular hydrogen transfer produces an alkene (routes 4a and 4b). At higher temperature, diene formation takes place via route 9.

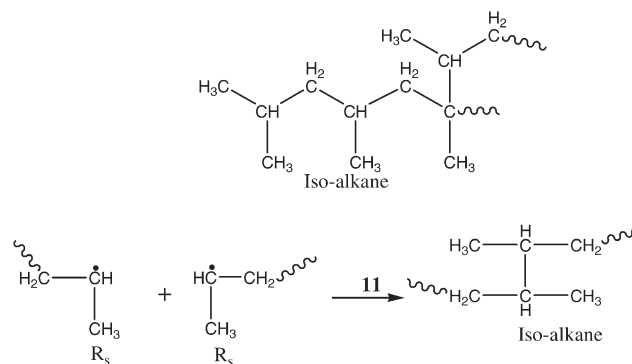
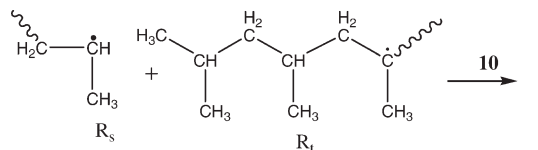


Higher molecular weight chain segments are more likely to yield diene³; hence, preferential formation of diene species at higher temperature may be expected.

Beyond 446°C, H-transfer reactions and β -scission reactions continue to take place, but radical recombination occurs to a greater degree, resulting in more of C24 and higher hydrocarbons.

Termination reactions involve the four families of radicals present in the system, *viz.*, R_p , R_s , R_t , and $R_{s'}$. Termination via radical recombination is more likely (because of higher concentration of the radicals in the pool) to take place at high temperature ($\geq 400^\circ\text{C}$), which justifies the increased yield of heavier hydrocarbons. Examples of termination via radical recombination reactions (between R_t and $R_{s'}$; and

two R_s radicals) are shown in the reaction schemes 10 and 11.



CONCLUSIONS

In this work, we report product distribution of volatile hydrocarbons (C5-C44) of PP over the temperature range of 200–600°C. Product analysis is an important aspect of thermal degradation study of polymers. In this work we have performed a temperature dependent pyrolysis product analysis of PP. We have also attempted to correlate the observed product evolution profile to possible reaction pathways. At low temperature (200–300°C), bond fission of weak links dominates the initiation of PP degradation; at temperatures above 300°C, C–C bond fission in general dominates the overall degradation process. Mode of termination reactions was found to have a pronounced effect on the yield of hydrocarbons. At low temperature of pyrolysis (200–300°C), abstraction is the preferred route for radical stabilization, which could be the reason for absence of heavy fragments in the pyrolyzate. At high temperature (>300°C), both radical recombination and β -scission play an important role, with termination by recombination having pronounced effect. Intramolecular hydrogen transfer justifies preferential formation of some hydrocarbons. Maximum amount of hydrocarbons were obtained at T_{max} . C5-C10 hydrocarbons were dominant species detected in the product mixture in our evaluation. Since the product evolution profile can be readily explained by well-established reaction pathways, a similar approach could also be adopted for other hydrocarbon polymers. The presented mechanistic views in this study can also be used for development of a polymer degradation kinetics model to predict evolution of products as a function of

conversion. Finally, one of the worthwhile goals to be pursued would be to extend such a study to pyrolysis of polymer mixtures; this would enable one to design operating conditions for targeted product profile.

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