Temperature-Dependent Pyrolytic Product Evolution Profile for Polyethylene Terephthalate

Ujwala Hujuri, Aloke K. Ghoshal, Sasidhar Gumma

Department of Chemical Engineering, Indian Institute of Technology Guwahati, Guwahati 781039, India
Correspondence to: S. Gumma (E-mail: s.gumma@iitg.ernet.in)

ABSTRACT: In this study, a detailed gas chromatographic study of pyrolysis products of polyethylene terephthalate (PET) has been carried out over a wide range of temperature (200–600°C). At low pyrolysis temperatures (200–300°C), yield of lighter hydrocarbons (C5–C10) is low; this gradually increases until maximum decomposition temperature (435°C) and decreases thereafter. At low temperature, PET essentially decomposes by ionic mechanism. However, at higher temperature, it may also proceed by radical mechanism. The following reaction types were considered to explain the decomposition mechanism of PET: (a) heterolytic (ionic) main-chain cleavage to form an olefin-end and an acid-end structure; (b) intra- or intermolecular ester-interchange reactions to yield cyclic oligomers; (c) intramolecular hydrogen transfer to form volatile products and regeneration of the acid-ends or, olefin-ends; (d) decarboxylation and intramolecular elimination of acetaldehyde, and acetylene; and (e) hydrogen abstraction and acetylene addition mechanism for the formation of polycyclic aromatic hydrocarbons. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 130: 3993–4000, 2013

INTRODUCTION

Polyethylene terephthalate (PET) packaging markets have seen a continuous growth over the last two decades. It first penetrated the carbonated soft drinks market and then took over the bottled water market. With the rapid increase in the consumption of PET, there is a parallel increase in the volume of waste PET. This has triggered the importance of the study of pyrolysis of PET, which can convert the plastic to useful hydrocarbons similar in properties to those present in conventional fuels.

PET is a aromatic polyester. The repeat unit consists of a benzene ring, two ester groups $(-\overset{\overset{O}{\parallel}}{C}-O-)$ along with two methylene ($-CH_2-$) groups. Owing to the presence of two heterogeneous linkages in the chain backbone, PET is thermally less stable than both low-density polyethylene (LDPE) and polypropylene (PP).[1,2] The structure of PET indicates possibility of production of significant amount of aromatic compounds as well as polycyclic aromatic hydrocarbons (PAHs). A careful investigation of its product distribution would help one to explain the possible decomposition routes, which is very important for better understanding of the pyrolysis process of PET. Literature reports that decomposition of PET produces about the same quantities of gas and liquid with a proportion of sol-

ids around 10%.[3,4] The gases contain carbon oxides (nearly 90%).[3] In the oils, benzene and toluene are the major components.[4]

In another study, Yoshioka et al.[5] carried out pyrolysis of PET in a fluidized bed reactor between 510 and 730°C, where pyrolysis gas consisted chiefly of CO_2 and CO (38–49%), the rest being liquids and a small amount of residue.

Montaudo et al.[6] studied the primary thermal decomposition mechanism of PET by direct pyrolysis mass spectrometry using negative chemical ionization. They found that cyclic oligomers, formed by intramolecular exchange (ionic) reactions are the primary pyrolysis products, which further decompose by β-H transfer reactions to generate open-chain oligomers with olefin and carboxylic end groups. Samperi et al.[7] in another study reported structural characterization of the products obtained by isothermal degradation of PET in the temperature range of 270–370°C. The results indicated the formation of cyclic oligomers which decompose at higher temperature. Anhydride-containing oligomers and acetaldehyde were detected at various temperatures. They also carried out few experiments by adding *p*-toluene sulfonic acid to PET, which induced a strong hydrolytic reaction with consequent increase of carboxyl end groups.

In another study by Martin-Gullon et al.,[8] different gases evolved from thermal decomposition of waste PET were analyzed by carrying out one pyrolysis run and one combustion run in a batch laboratory scale tubular reactor at 850°C at fuel-rich conditions, where an appreciable amount of PAH was detected.

Holland and Hay[9] studied the thermal degradation of PET by thermal analysis-Fourier transform infrared spectroscopy, and the effect of comonomer (viz. diethyelene glycol and isophthalic acid) modifications of PET on thermal stability. They observed that these comonomer units promoted thermal degradation through increased chain flexibility and more favorable bond angles, respectively. Infrared analysis indicated that the residue obtained after pyrolysis, consisted of interconnected aromatic rings.

Sovová et al.[10] in their study, compared the products resulting from uncontrolled combustion of PET to that obtained from controlled decomposition (500°C) and combustion processes (800°C) using different techniques, namely high-resolution Fourier transform infrared spectroscopy, selected ion flow tube mass spectrometry, and gas chromatography (GC) mass spectrometry. They have observed that products resulting from uncontrolled burning in air were comparable to those resulting from decomposition at 500°C. The abundance of products at 800°C was found to be lower than that at 500°C.

Thus, from the forgoing discussion on the available studies on PET, it can be seen that there is a dearth of references in the area of product distribution from PET over a wide range of decomposition temperatures. Moreover, product evolution at different temperatures has also not been linked to the mechanistic aspects of decomposition in most of the reported studies. In this perspective, it is necessary to carry out a systematic investigation on product distribution from pyrolysis of PET at different temperatures.

In our earlier studies,[1,2] the pyrolysis–GC studies of LDPE and PP over a wide range of temperature were reported. It was observed that both the polyolefins degrade over a wide range of temperature (200–600°C) and produce a homologous series of hydrocarbons; suitable reaction pathways were also proposed to explain the formation of hydrocarbon products (C5–C44).

Following a similar approach, a detailed product distribution study was carried out for C5–C44 hydrocarbons from pyrolysis of PET over a wide range of temperature (200–600°C). To the best of our knowledge, such kind of studies has not been reported in the literature so far. The usefulness of this study lies in the fact that the information generated can be utilized for understanding the underlying reaction pathways. In this study, decomposition of PET has been carried out in a thermogravimetric analysis (TGA) and product analysis is carried out in a GC equipped with FID detector. Evolution of hydrocarbons (C5–C44) has been monitored at six different temperatures starting from 200°C (where there is a negligible product formation) through 600°C (end of degradation). The GC results are used to study the product distribution and correlate the same with the decomposition mechanism of PET (including those available in the literature).

EXPERIMENTAL

Materials

PET used in this study was virgin PET (AS-40, bottle grade) supplied by South Asian Petrochem, India. It has a melting point of 248.4°C, heat of fusion of 44.91 J/g, and a percentage crystallinity of 39.05%.[11] Virgin PET was used in this study to eliminate the effects of different additives and/or impurities that may be present in waste sample. 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 (mesh size, −25/+35), transferred to a 150-μL 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[e]) in an argon atmosphere (flow rate, 40–50 mL/min). The sample was heated 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 taken to GC for analysis.

GC Calibration and Product Analysis

The GC experiments were performed using a Varian 450 GC with an FID detector. An ultra low-bleed Factor Four-capillary column VF-200 ms (Varian) (30 m length, 0.25 μm film thickness, 0.25 mm ID) composed of trifluropropyl methyl stationary phase was used for the separation. Carrier gas (N$_2$) flow rate of 1.5 mL/min was used and the column oven program had an isothermal segment at 30°C with hold time of 6 min, ramp heating from 30 to 50°C at a rate of 0.6°C/min, ramp heating from 50 to 300°C at a rate of 10°C/min.

In an independent preliminary calibration procedure, two quantitative reference petroleum standards (ASTM D3710 Quantitative Calibration Mix containing C5-C15 hydrocarbons and ASTM D5442 Qualitative Retention Time Mix containing C16-C44 hydrocarbons) supplied by Sigma Aldrich, India, were injected into the GC. The analysis of these standards yielded retention times corresponding to C5–C44 hydrocarbons. These retention times were used as a benchmark for identifying the carbon number corresponding to the peaks obtained in chromatogram of the product evolved during pyrolysis experiments.

Column oven program and other parameters were set so as to optimize separation between the different hydrocarbon species (C5–C44) present in the standards used for calibration. However, this resulted in long elution times for higher hydrocarbons from the GC column. Further, for the detection of PAHs, a Polynuclear Aromatic Hydrocarbon Mix standard (Z-014G) supplied by Rankem Chemicals, India, was used which aided in the determination of the retention time range during which PAHs evolve. The boiling temperature for PAHs ranges from 218°C (for naphthalene, a C10 compound) to 536°C (for indeno(1,2,3-cd)pyrene, a C22 compound), which corresponds to their aliphatic counterparts having carbon number C12 (boiling temperature, 216°C) and C40 (boiling temperature, 527°C).
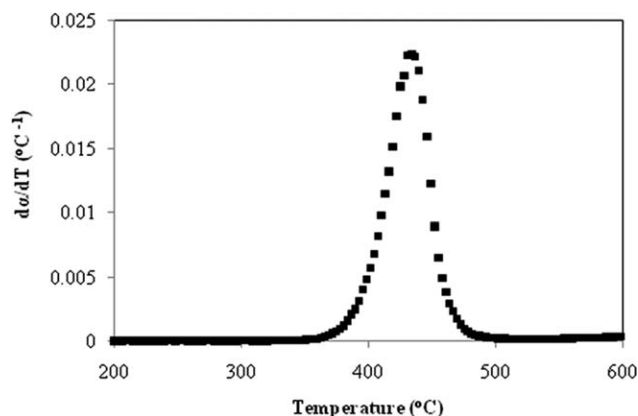
Figure 1. DTG curve of PET (heating rate, 10°C/min; Ar flow rate, 40 mL/min).

Thus, retention times corresponding to C12 and C40 aliphatic hydrocarbons should be comparable to their C10 and C22 aromatic counterparts, respectively.
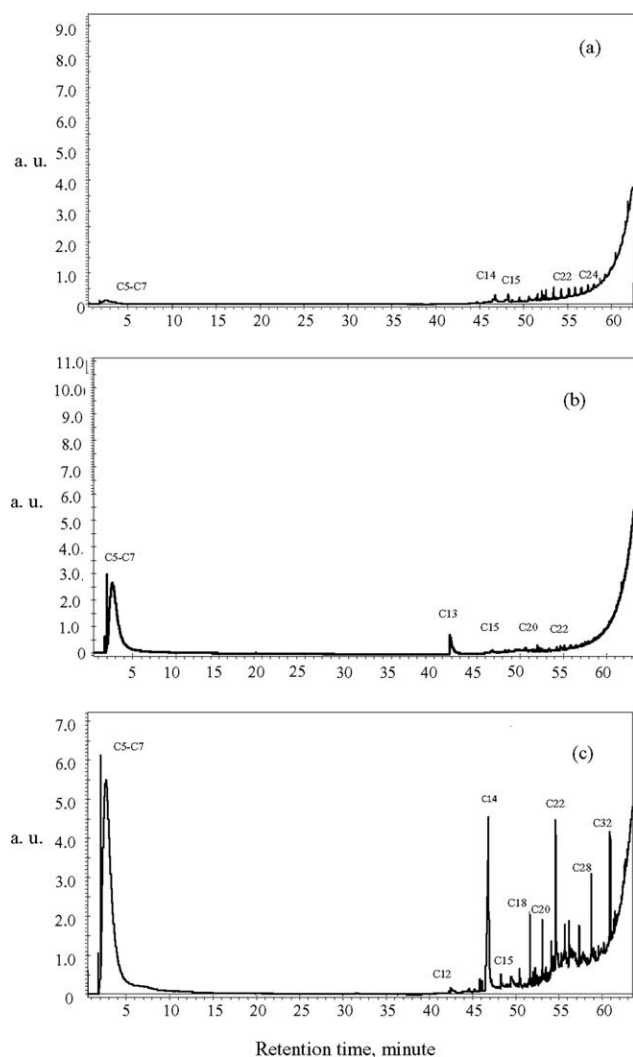

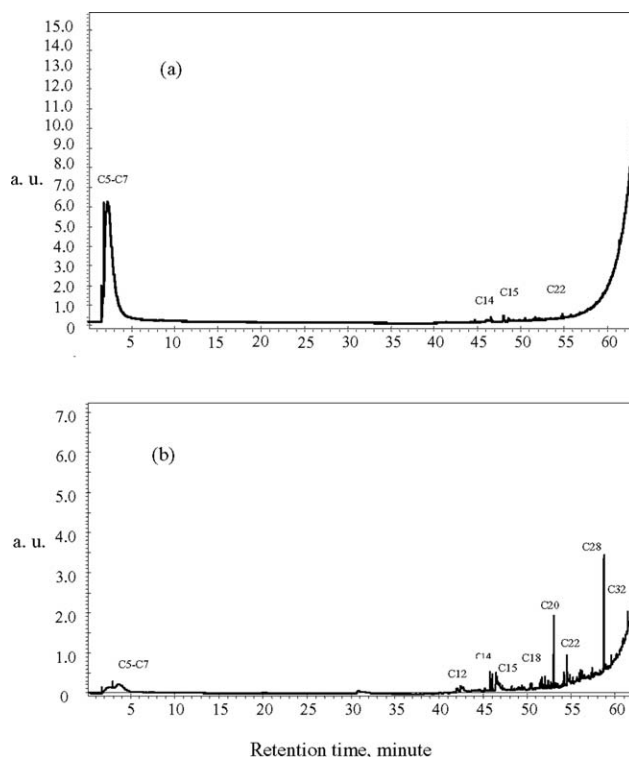**Figure 2.** Pyrogram of PET obtained at (a) 300°C, (b) 400°C, and (c) 435°C (T_{max}).

Figure 3. Pyrogram of PET obtained at (a) 500°C and (b) 600°C.

During the product analysis, 1 mL of sample evolved from the TGA at temperature of interest was drawn into a gas tight syringe (Hamilton, Gas-tight, Model: 1005) and injected into the GC.

RESULTS AND DISCUSSION

Product Analysis

A typical derivative thermogravimetric (DTG) curve for rate of decomposition $d\alpha/dT$ (where $\alpha = (W_0 - W)/(W_0 - W_\infty)$, W_0 is the initial weight of the sample, W is the sample weight at any temperature, T, and W_∞ is the sample weight at 600°C) of PET is shown in Figure 1. It is evident from this figure that maximum decomposition temperature (T_{max}) for PET is about 435°C.

Figure 2(a–c) show pyrograms of the pyrolysis products of PET obtained at 300°C, 400°C, and T_{max}, respectively. Figure 3(a,b) shows pyrograms corresponding to 500 and 600°C. Pyrolysis product of PET contains a wide array of hydrocarbons, including mostly aromatic hydrocarbons with the *p*-phenylene group ($-C_6H_4-$) as an inherent part, indicative of the structure of the original polymer.

At 300°C, C5–C7 fraction produced is insignificant. Other hydrocarbons which are obtained in traces are C14, C15, C16, C18, C20, C22, C24, C26, and C28, some of which are identified in the figure. Others, which are not marked, fall in between the identified peaks. Figure 2(b) shows the pyrogram obtained at 400°C. As it is shown in Figure 2(b), there is a marked increase in the evolution of C5–C7 hydrocarbons, and C5–C7 production overshadows the production of other hydrocarbons.
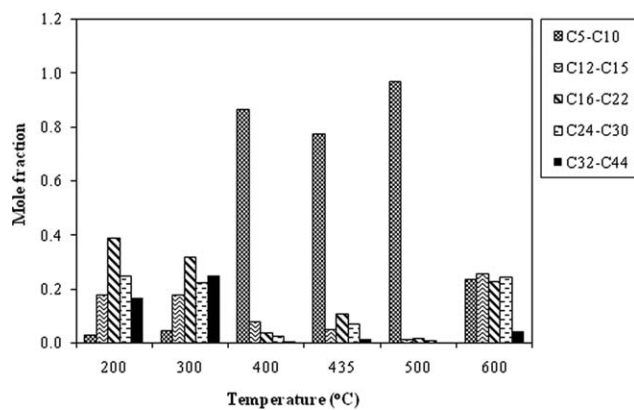
Figure 4. Mole fractions of different hydrocarbon fractions (C5–C44) obtained from pyrolysis of PET at different temperatures.

Figure 2(c) shows the pyrogram at T_{max} (i.e., at 435°C), marked by sharp and distinct peaks. Clearly, a wide range of hydrocarbons evolve from the pyrolysis. The oligomers which were formed at lower temperatures (≤300°C) decompose further, resulting in the formation of low-boiling fractions. The first broad peak represents C5–C7 en masse. Given the structure of PET, benzene (C6), toluene (C7), terephthalic acid (TPA) (C8), monoethenyl terephthalate (C10), and diethenyl terephthalate (C12) are expected to be the major products at this temperature, whereas the oligomers with carboxyl and olefin ends are regenerated in these processes, which keep the degradation process alive. The other hydrocarbons, detected, are C12, C13, C15, C16, C18, C20, C22, C24, C28, C30, and C32, which are expected to be mostly aromatic. As considerable amount of benzene is likely to evolve at this temperature, the formation of PAHs cannot be ruled out at this temperature (as will be explained later). As the retention times for C12–C44 hydrocarbons are similar to PAHs in C10–C22 range, it is likely that pyrograms shown in Figure 2(c) also include PAHs such as naphthalene (C10), acenaphthylene (C12), anthracene (C14), pyrene (C16), and so on.

Figure 3(a) shows the chromatogram of PET at 500°C. At this temperature, evolution of C5–C7 hydrocarbons is high; however, it is less than that at T_{max}. Evolution of other hydrocarbons (C12 and higher) significantly decreases at this temperature. At 600°C, macromolecular chain considerably reduces in length as conversion is nearly complete at this temperature (Figure 1). At 600°C [Figure 3(b)], C5–C7 hydrocarbons continue to evolve, but their amount decreases as compared to that at T_{max}. The other aromatic/aliphatic hydrocarbons evolved are C12, C14, C15, C18, C20, C22, C28, and C32. The heavier hydrocarbons C36, C40, and C44 are also found in traces; the peak intensity being very small, they cannot be labeled in the pyrogram. However, their formation has been confirmed from GC results. The products might also encompass PAHs having C12, C13, C16, C20, and C22 species.

Figure 4 shows the mole fractions of C5–C44 hydrocarbons contained in the pyrolysis product stream as a function of temperature. At 200°C, the formation of C16–C22 and C24–C32 fractions is relatively more as compared to that of the lighter

components. C12–C15 and C32–C44 has almost an equal share in the total product yield, whereas yield of C5–C10 is quite less. The negligible evolution of C5–C10 fraction can be attributed to the extra stability of the polymer owing to the resonance-stabilized structures in the chain backbone, which needs higher energy to overcome the attractive forces. The detectable amounts of higher fractions are possibly owing to the cyclic oligomers (as will be explained later).

At 300°C, a slight increase in the production of C5–C10 hydrocarbons is observed and production of C32–C44 also increases, whereas C16–C22 and C24–C30 diminishes in amount. As temperature proceeds, intensity of cracking reactions increases, resulting in increased amount of lighter hydrocarbons. Thus, as we go from 300 to 400°C, there is considerable increase in the evolution of C5–C10. At 400°C, the relative production of different hydrocarbons decreases in the order C12–C15>C16–C22>C24–C30>C32–C44. At 435°C, which is the maximum decomposition temperature, yield of C5–C10 fraction continues to be the dominant product fraction. The relative production of different hydrocarbons follows the order C16–C22>C24–C30>C12–C15>C32–C44. C5–C10 continues to be the highest product fraction at 500°C, and the formation of other fractions is insignificant as compared to that of C5–C10. At 600°C, relative production of the first four fractions (i.e., C5–C10, C12–C15, C16–C22, and C24–C32) is more or less equal, whereas the share of the C32–C44 fraction is considerably less.

Mechanistic Analysis

In our earlier communications,[1,2] we have presented mechanistic views of thermal decomposition of LDPE and PP, both of which are addition polymers which degrade by free-radical mechanism. There is a difference between the modes of decomposition of addition polymers (LDPE and PP) from those of condensation polymers (PET). Addition polymers contain aliphatic hydrogen atoms along the chain backbone, which are easily transferred after homolytic bond cleavage in the temperature range of 200–500°C. The majority of addition polymers undergo thermal degradation through the formation of macroradicals, which are very reactive species undergoing decomposition by bond cleavage. PET is a condensation polymer of TPA and ethylene glycol. For commercial practices, TPA is often replaced by dimethyl terephthalate and ethylene glycol by diethylene glycol. Condensation polymers can be regarded as a sequence of monomer units containing functional groups immobilized into the polymer structure. Their decomposition pathways are often dominated by the polarity and reactivity of the functional groups within their structure, and their thermal degradation reactions are ionic and selective, rather than radical and unselective. These ionic pathways typically occur at temperatures (150–300°C), below those of typical free-radical degradation reactions.

There exist considerable controversies among the researchers regarding the decomposition route of PET.[12,13] Literature reports that thermal decomposition of PET does not involve radical (homolytic) pathway.[13] However, if the polymer is subjected to higher temperatures, radical reactions are likely to prevail. The proposed reaction pathway separately takes into account the formation of cyclic oligomers, volatile

hydrocarbons, and PAHs and is considered to represent its product distribution.

The structural repeat unit of PET can be represented by the following formula.

where, Ph: ⬡
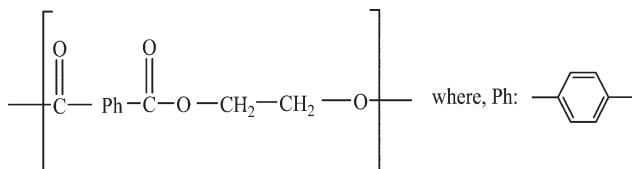
In pure PET, three general structures are present: (i) "in chain" structures as depicted above by the structural formula, (ii) "hydroxyl ends," and (iii) carboxyl ends.[14] The latter two result owing to the nature of the polymerization reaction. The predominant structure will be the "in chain" one, and the other two will be in a much lesser extent.

As it has already been explained that cyclic oligomers (dimers or trimers, as a weak link in the PET chain) might evolve at low temperatures (200–300°C). These are possibly formed during polymerization process and remain as weak links in the polymer molecule. Usually, polymers prepared by condensation polymerization contain small amounts of small cyclic molecules along with the much higher molecular weight of linear chains.[13] The equilibrium content of cyclic oligomers in PET is around 2%.

Similarly, there are references in the literature which have confirmed the contribution of weak links in early decomposition in some plastics. Richards and Salter[15–17] in their study evaluated thermal degradation of PS by using poly(α-methylstyrene) as a radical producing agent and confirmed the contribution of these weak links in initiating the degradation at otherwise stable temperatures.

Moreover, intramolecular ester exchange reaction might also lead to the formation of cyclic as well as linear oligomers. This justifies the evolution of product fractions observed at low temperatures. As shown in *Reaction Scheme 1(a)*, a macromolecular chain of PET might undergo intramolecular ester exchange reaction, giving rise to a cyclic dimer (C20). This involves attack of hydroxyl ends on the inner ester groups of the PET chain.[5] In a similar way, the formation of a cyclic trimer (C30) and tetramer (C40) is shown in *Reaction Scheme 1(b,c)*, respectively.
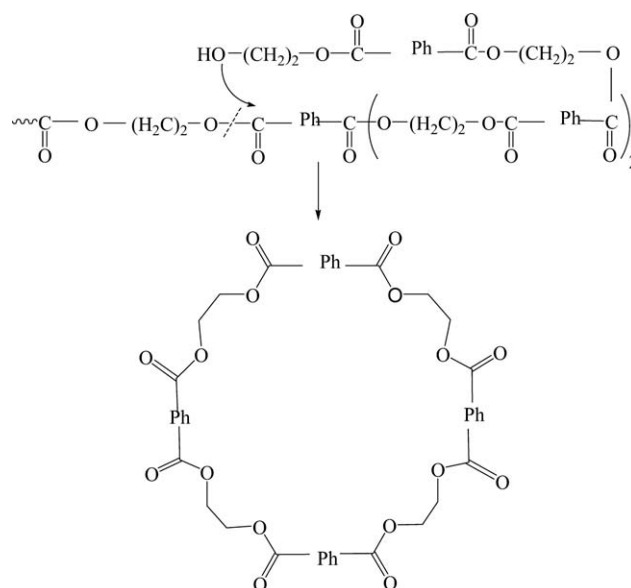

Cyclic dimer
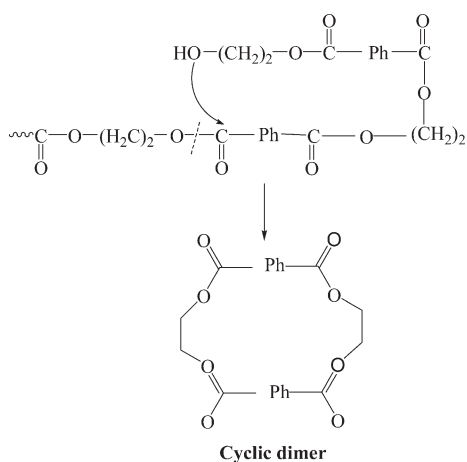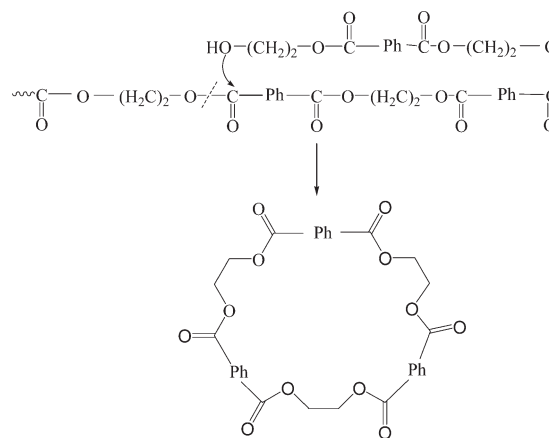
Reaction scheme 1(a)

Cyclic Trimer
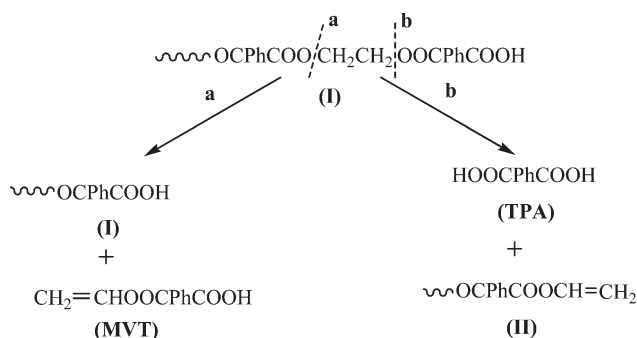
Reaction scheme 1(b)

Reaction scheme 1(c)

Initial decomposition of PET occurs via a six-membered ring intermediate in which hydrogen from a β-carbon (to ester group) is transferred to the ester carbonyl, followed by scission at the ester links, resulting in carboxylic acid end group (**I**) and vinyl end group (**II**) as shown in the *Reaction Scheme 2*.[18–20]
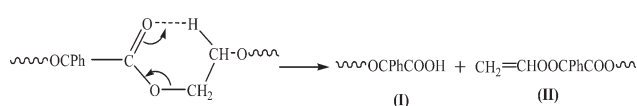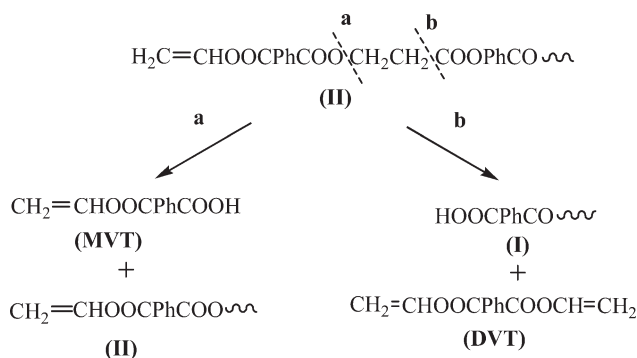

Reaction scheme 2

The carboxyl end unit (**I**) may undergo decomposition by β-hydrogen transfer by two routes as shown in *Reaction Scheme 3*. The route **3a** leads to the formation of monovinyl terephthalate (**MVT**). **I** is regenerated in the process. The route **3b** leads to the formation of **TPA** (C8), and Species **II**.

Reaction scheme 3

Similarly, the olefin end unit (**II**), thus produced in *Reaction Scheme 2*, might undergo decomposition via two routes, **4a** and **4b** (as shown in *Reaction Scheme 4*). The route **4a** leads to the formation of **MVT** (C10), and the Species **II**, whereas route **4b** leads to the formation of divinyl terephthalate (**DVT**) (C12), and the Species **I**.
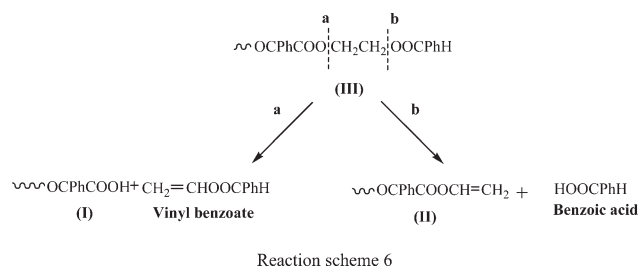

Reaction scheme 4

With increase in temperature, evolution of C5–C10 increases. As already stated, this could be owing to the formation of benzene, toluene, benzoic acid, styrene, vinyl benzoate, ethyl benzene, and so on. The following reactions (*Reaction Schemes 5–12*, discussed subsequently) explain the formation of these hydrocarbons. Literature reports significant production of CO_2 from pyrolysis of PET at higher temperature (beyond 300°C).[4] This may take place from a carboxyl end group via *Reaction Scheme 5*.
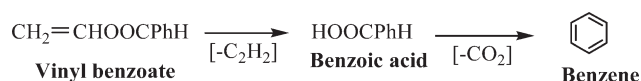

Reaction scheme 5
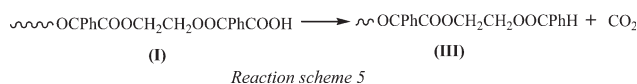
This path also produces a phenyl end group, which subsequently undergoes β-hydrogen transfer, following a six-membered rearrangement of the ester linkage, to generate vinyl benzoate and benzoic acid, following route **6a** and **6b** as shown in *Reaction Scheme 6*. In this process, Species **I** and **II** get regenerated with reduced chain length. Thus, the decomposition process of PET continues till it leaves out a carbonaceous residue.
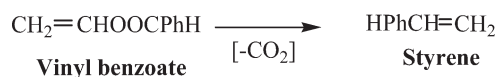

Reaction scheme 6

Vinyl benzoate produced via route **6a**, also leads to the formation of benzoic acid as shown in *Reaction Scheme 7*, which is reportedly another major product of PET decomposition.[18] Benzoic acid can undergo decarboxylation to yield benzene.
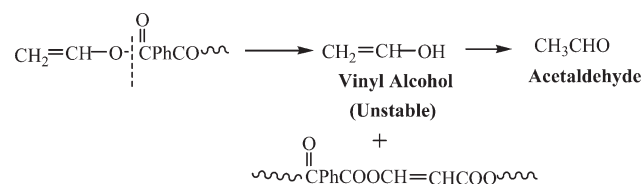

Reaction scheme 7

On the other hand, decarboxylation of vinyl benzoate leads to the formation of styrene (*Reaction Scheme 8*).
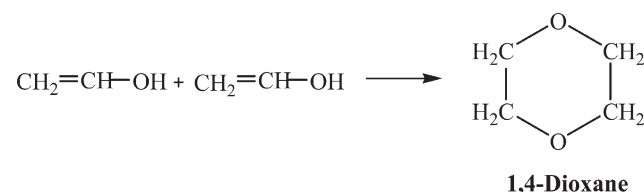

Reaction scheme 8

The olefin end group (**II**) undergoes scission at the ester link and gives rise to vinyl alcohol, which is unstable and possibly rearrange to give acetaldehyde (*Reaction Scheme 9*). The broad peak corresponding to C5–C7 might also include these C2 fractions [Figure 2(b)].
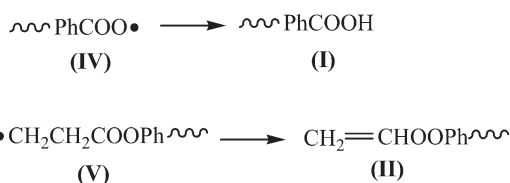

Reaction scheme 9

Reaction scheme 10

In the discussion so far, we have not accounted for the homolytic (free radical) scission of the PET chain. However, at high temperatures (≥400°C), homolytic scission might take place.[21–23] The weakest link in the PET structure is possibly the carbonyl–oxygen–methylene sequence ($COOCH_2CH_2$) in the repeat unit,

which might homolytically cleave in the following two ways (*Reaction Schemes 11 and 12*):

Reaction scheme 11

Reaction scheme 12
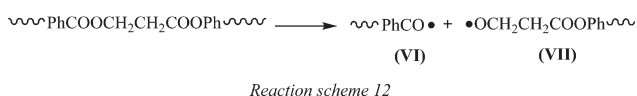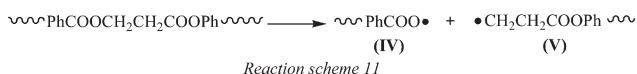
After the formation of these free radicals, the immediate next step will be hydrogen abstraction, intra- and intermolecular hydrogen transfer followed by β-scission, or recombination of the radicals, so as to generate stable molecules. As an example, the free-radical **IV** might abstract a hydrogen atom to form an acid end group, thus regenerating **I**, whereas the radical **V** might undergo intramolecular hydrogen transfer, forming a vinyl end group, thus regenerating **II** (*Reaction Scheme 13*).
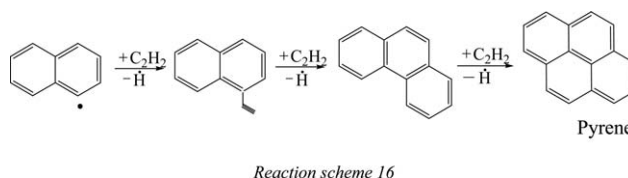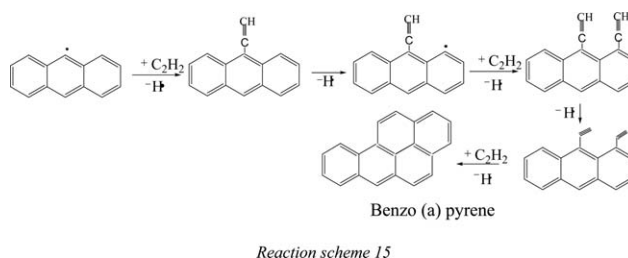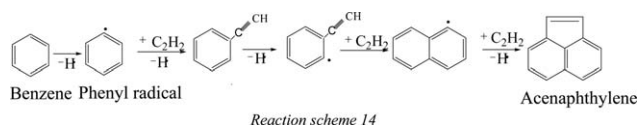

Reaction scheme 13

A carbonaceous residue is obtained at the end of each degradation experiment, which constitutes approximately 10–12% of the total weight of the starting polymer. These could be owing to the formation of PAHs, which are compounds with fused aromatic rings. Formation of PAHs is possible only at higher temperatures (>400°C), as discussed below. Formation of benzene is crucial for the inception and growth of PAHs. Literature suggests that once benzene is available, there are three possible routes suggested in the literature, by which larger PAHs may grow.

The first route as suggested by Frenklach et al.,[24] involves sequential hydrogen abstraction and C_2H_2 (acetylene) addition (referred to as hydrogen abstraction C_2H_2 addition [HACA] mechanism). The second route as suggested by Mukherjee et al.[25] involves direct polymerization of PAHs through the initial formation of PAH dimers which further proceeds through ring–ring condensation of higher PAHs. This route leads to the formation of high-molecular-weight PAHs. The third route as proposed by Krestinin et al.[26] involves the polymerization of polyynes (a group of organic compounds with alternating single and triple bonds) on a surface radical site and its transformation into aromatic structures, leading to the breeding of radical sites and rapid growth. Polyynes are found in interstellar molecular clouds where hydrogen is scarce. In our study, however, we have considered only the first two routes to explain the formation of PAHs studied in this evaluation, as the formation of polyynes is not likely under the present experimental conditions.[27]

At low temperature (200–300°C), PAHs are not formed, as at such low temperatures benzene does not evolve. After the formation of benzene (following *Reaction Schemes 6 and 7* mentioned

earlier), a hydrogen radical from benzene is stripped off releasing highly reactive phenyl radical.[28] This serves as the initiation step for all the subsequent reactions to follow, leading to the formation of PAH by HACA route. Following reactions (*Reaction Schemes 14–16*) have been proposed to explain the formation of some specific PAHs such as acenaphthylene ($C_{12}H_8$), benzo(a)-pyrene ($C_{20}H_{12}$), and pyrene following HACA mechanism.

Reaction scheme 14

Reaction scheme 15

Reaction scheme 16

HACA pathways, however, cannot predict some of the PAHs like benzofluoranthene. *Reaction Scheme 17* explains the dimerization and coalescence of two biphenyls, leading to the formation of benzofluoranthene.[26]
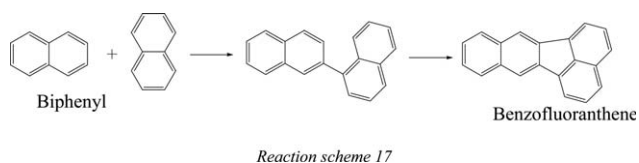
Reaction scheme 17

Cyclodehydrogenation of two toluene molecules results in the formation of anthracene (*Reaction Scheme 18*).

Reaction scheme 18
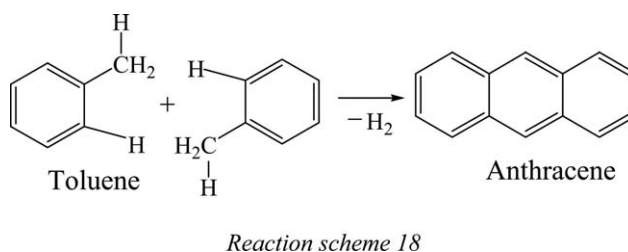
CONCLUSIONS

Pyrolysis of PET involves a network of heterolytic and homolytic chain scission reactions. Products obtained range from

simple acetylene gases to complex PAHs which are solids. At low temperature (200–300°C), its thermal degradation mainly occurs by heterolytic or ionic mechanism which explains the formation of benzene, TPA, MVT, acetaldehyde, CO_2, as well as cyclic dimers and trimers. Ionic mechanism, however, cannot explain the formation of most of the PAHs. Benzene is inevitable for their inception, and radical reactions could explain their formation following HACA routes. At higher temperature (at or above 400°C), radical reactions come into play, which lead to the formation of PAHs along with other species. It is worth mentioning here that PAHs fall under the class of persistent organic pollutants, some of which are termed as carcinogenic and hence are completely undesirable in any product stream routed to atmosphere. Thus, pyrolysis of PET should be carefully carried out so as to avoid the formation of PAHs. The formation of dioxin, which is owing to dimerization of vinyl alcohol, is a secondary reaction, the primary reaction being acetaldehyde formation. Thus, dioxin concentration in the product stream is low enough so as not to cause any catastrophic damage to the environment. The carbonaceous charred product, obtained at the end can be upgraded to obtain activated carbon. Thus, pyrolysis of PET, if conducted under controlled environment, yield a host of important petrochemicals (benzene, toluene, xylene, etc.) as well as petrochemical feedstock (DVT, MVT, etc.), which has got tremendous market value.

REFERENCES

1. Hujuri, U.; Ghoshal, A. K.; Gumma, S. *Waste Manage.* **2010**, *30*, 814.

2. Hujuri, U.; Ghoshal, A. K.; Gumma, S. *J. Appl. Polym. Sci.* **2011**, *119*, 2318.

3. Williams, P. T.; Williams E. A. *J. Energy Inst.* **1998**, *71*, 81.

4. Kaminsky, W.; Sinn, H. In Recycling and Recovery of Plastics 1996; Brandrup, H. J., Bittner, M., Michaeli, W., Menges, G., Eds.; Hanser: München, **1996**, p 434.

5. Yoshioka, T.; Grause, G.; Eger, C.; Kaminsky, W.; Okuwaki, A. *Polym. Degrad. Stab.* **2004**, *86*, 499.

6. Montaudo, G.; Puglisi, C.; Samperi, F. *Polym. Degrad. Stab.* **1993**, *42*, 13.

7. Samperi, F.; Puglisi, C.; Rossana, A.; Montaudo, G. *Polym. Degrad. Stab.* **2004**, *83*, 3.

8. Martin-Gullon, I.; Esperanza, M.; Font, R. *J. Anal. Appl. Pyrol.* **2001**, *58–59*, 635.

9. Holland, B. J.; Hay, J. N. *Polymer* **2002**, *43*, 1835.

10. Sovová, K.; Ferus, M.; Matulkova, I.; Španìl, P.; Dryahina, K.; Dvoøák, O.; Civis, S. *Mol. Phys.* **2008**, *106*, 1205.

11. Saha, B.; Ghoshal, A. K. *Chem. Eng. J.* **2005**, *111*, 39.

12. Levchik, S. V.; Weil, E. D. *Polym. Adv. Technol.* **2004**, *15*, 691.

13. Montaudo, G.; Puglisi, C. In Mass Spectrometry of Polymers, 1st ed.; Montaudo, G., Lattimer, R. P., Eds.; CRC Press: Florida, **2001**.

14. Fairgrieve, S. Degradation and Stabilization of Aromatic Polyesters; Smithers Rapra: Shawbury, **2009**.

15. Richards, D. H.; Salter, D. A. *Polymer* **1967**, *8*, 127.

16. Richards, D. H.; Salter, D. A. *Polymer* **1967**, *8*, 139.

17. Richards, D. H.; Salter, D. A. *Polymer* **1967**, *8*, 153.

18. Buxbaum, L. H. *Angew. Chem. Int. Ed.* **1968**, *7*, 182.

19. Zimmermann, H. In Developments in Polymer Degradation; Grassie, N., Ed.; Elsevier Applied Science Publishers Ltd.: London, **1984**; Vol. *5*.

20. McNeill, I. C.; Bounekhel, M. *Polym. Degrad. Stab.* **1991**, *34*, 187.

21. Kalontarov, I. Y.; Niyazi, F. F.; Chajko, Y. V. *Int. J. Polym. Mater.* **1990**, *13*, 53.

22. Niyazi, F. F.; Kasymova, E. I.; Kalontarov, I. Y.; Abdullaev, K. A. *Int. J. Polym. Mater.* **1993**, *19*, 231.

23. Pasquale, G. D.; Pollicino, A.; Recca, A.; Bottino, F. A.; Sandri, M. *Polymer* **1996**, *37*, 703.

24. Frenklach, M.; Clary, D.; Gardiner, W. C.; Stein, S. E. In Twentieth International Symposium on Combustion, The Combustion Institute, Pittsburgh, **1984**, p 887.

25. Mukherjee, J.; Sarofim, A. F.; Longwell, J. P. *Combust. Flame* **1994**, *96*, 191.

26. Krestinin, A. V.; Kislov, M. B.; Raevskii, A. V.; Kolesova, O. I.; Stesik, L. N. *Kinet. Catal.* **2000**, *41*, 90.

27. Cherchneff, I. In PAHs and the Universe; Joblin, C., Tielens, A. G. G. M., Eds., EAS Publication Series: Basel, **2010**.

28. Lam, F. W. The formation of aromatic polycyclic aromatic hydrocarbons and soot in a jet-stirred plug-flow reactor, PhD Thesis, Massachusetts Institute of Technology, **1988**.