



PT-1

POLYETHYLENE TEREPHTHALATE HYDROLYSIS BY γ -RADIATION

Naima A. El-Gendy* and Abdel-Mohty. A.**

ABSTRACT

Flakes of polyethylene terephthalate (PET) alkaline hydrolyzed by sodium hydroxide were subjected to gamma rays. Some parameters were studied; irradiation doses (10 - 60 kGy), NaOH concentrations (1 - 4 M) and PET particle size (300 and 600 μm). The reaction time (60 – 540 min) required for sodium hydroxide/methanol hydrolysis of PET was optimized to investigate the products were obtained. Optimal dose able to converts PET into dimethyl terephthalate (DMT) was 20 kGy. DMT was analyzed qualitatively. The alkaline depolymerization of polyethylene terephthalate (PET) has been evaluated by HPLC.

Keywords

PET / Recycling / γ -Ray / Hydrolysis.

* Department of Polymer, National Center for Radiation Research and Technology, Egypt

** Hot Laboratories Center, Atomic Energy Authority, P.No.13759, Egypt.

1. Introduction

One of the known polymer condensation is polyethylene terephthalate PET which known as Mylar film or Dacron fiber. This fiber has a wide range of use in our life, from the drinking and Juice bottles in the children hand's to satellite in the sky. The product is a worth to the industry fields all over the world. It has many advantages; strong, flexible and resistance to degradation. PET is naturally adsorbs water from its surroundings. However when this "damp" PET is then hydrolysis takes place between the water and the PET which reduces its molecular weight and its physical properties. With increasing PET consumption, its recycling for the preservations of resources and protection of the environment is required [1]. Chemical recycling of PET is discussed in detail leads to the formations of the raw materials (monomers) from which polymers are made. Chemical recycling processes for PET are divided as follows: (i) glycolysis, (ii) methanolysis, (iii) hydrolysis processes (iv) other processes. The main depolymerization processes [2-7] that have reached commercial maturity are glycolysis and methanolysis [8,9]. Essentially, glycolysis involves the insertion of ethylene glycol (EG) or diethylene glycol and propylene glycol in PET synthesis and its oligomers. The PET recycles have been studied by several investigators and reviewed by others [10-20]. The main advantages of alkaline methanolysis and hydrolysis methods are that they can be easily integrated into a conventional PET production plant and recover terephthalic acid (TPA). Further, an installation of a methanolysis unit can be located in the polymer production line, since the dimethyl terephthalate (DMT). Also, EG and methanol can be easily recovered and recycled. In this way, waste PET arising in the production cycle is utilized and the monomers recovered can be reused in the manufacture of a full value polymer. Disadvantages of the method include the high cost associated with the separation and refining of the mixture of the reaction products (glycols, alcohols and phthalate derivatives) and if water enters into the process it poisons the catalyst and forms various azeotropes [2,21]. Other disadvantages are associated with the trend of all new PET production process to use TPA instead of DMT as a new material. The conversion of DMT produced by hydrolysis to TPA adds considerable cost in the methanolysis process. Alkaline hydrolysis of PET is usually carried out with the use of an aqueous alkaline solution of NaOH. The reaction products are EG and the disodium terephthalate salt, TPA-Na. The mixture is heated up to 340 °C to evaporate and recover EG. Pure TPA can be obtained by neutralization of the reaction mixture with a strong mineral acid. Alkaline decomposition in aqueous solutions has been reported [21,22]. The addition of dimethyl- sulphoxide (DMSO) is suitable to PET as nearest it to solubility parameter [23]. In this work, the effect of gamma radiation on PET studied; during alkaline hydrolysis to investigate the production and byproduct which produces and compare with the alkaline hydrolysis for PET by reflux [24].

The aim of this work is investigate the products and byproducts which produces by gamma - ray and by reflux for the alkaline hydrolysis of PET using HPLC.

2. Experimental

Polyethylene terephthalate PET flakes free other plastics were prepared from used PET bottles, taken from post-consumer soft-drink bottles. The bottles were cut and fed to a rotary cutter with two sizes of 0.3 mm. and 0.6 mm. NaOH, CH₃OH and dimethylsulphoxide DMSO were obtained from Aldrich Germany. The volume ratio for NaOH: CH₃OH was 70:30 % and 1 ml of DMOS. Irradiations were carried out using a ⁶⁰Co gamma source (in National Center for Radiation Research and Technology, AEA, Egypt). The irradiation process was carried out at the ambient temperature (45 ± 1 °C in the chamber). Dose rate studies were carried out

using lead attenuates (50% and 75% attenuation) and the dose was determined by Fricke Dosimeter.

High Performance Liquid Chromatography (HPLC) Analysis

The solid samples were analyzed by HPLC (in Hot Laboratories Center, AEA, Egypt) using a Merck-Hitachi high performance liquid chromatography (HPLC), Germany, equipped with a Nucleosil C₈(250 x4 mm, 5 μ m) columns, L-6000 pump, L-4000 UV-detector set at 254 nm and D-2500 chromato-integrator. The HPLC procedure was carried out as follows: 20 mg/l, sample solution for analysis was prepared by dissolving a certain amount of the dried solid product in a 70: 30 (v/v) methanol/ water solution, which was also used as mobile phase with a flow rate of 1 ml/min. The temperature of the column was fixed at 25 \pm 1 $^{\circ}$ C.

3. Results and discussion

Waste PET flakes were first hydrolyzed in sodium hydroxide and CH₃OH to yield the disodium salt terephthalate salt TPA-Na₂ was continued to yield the dimethyl terephthalate (DMT) according to the chemical reaction, which was then acidified to convert to terephthalic acid (TPA). In this work DMSO is used to solublize the expected separated TPA from the surface of PET [22,23]. Also methanol accelerates the reaction (Table 1):

1. PET Alkaline Hydrolysis (NaOH/CH₃OH) by γ -Radiation

1.1. Weight decrease in PET Flakes

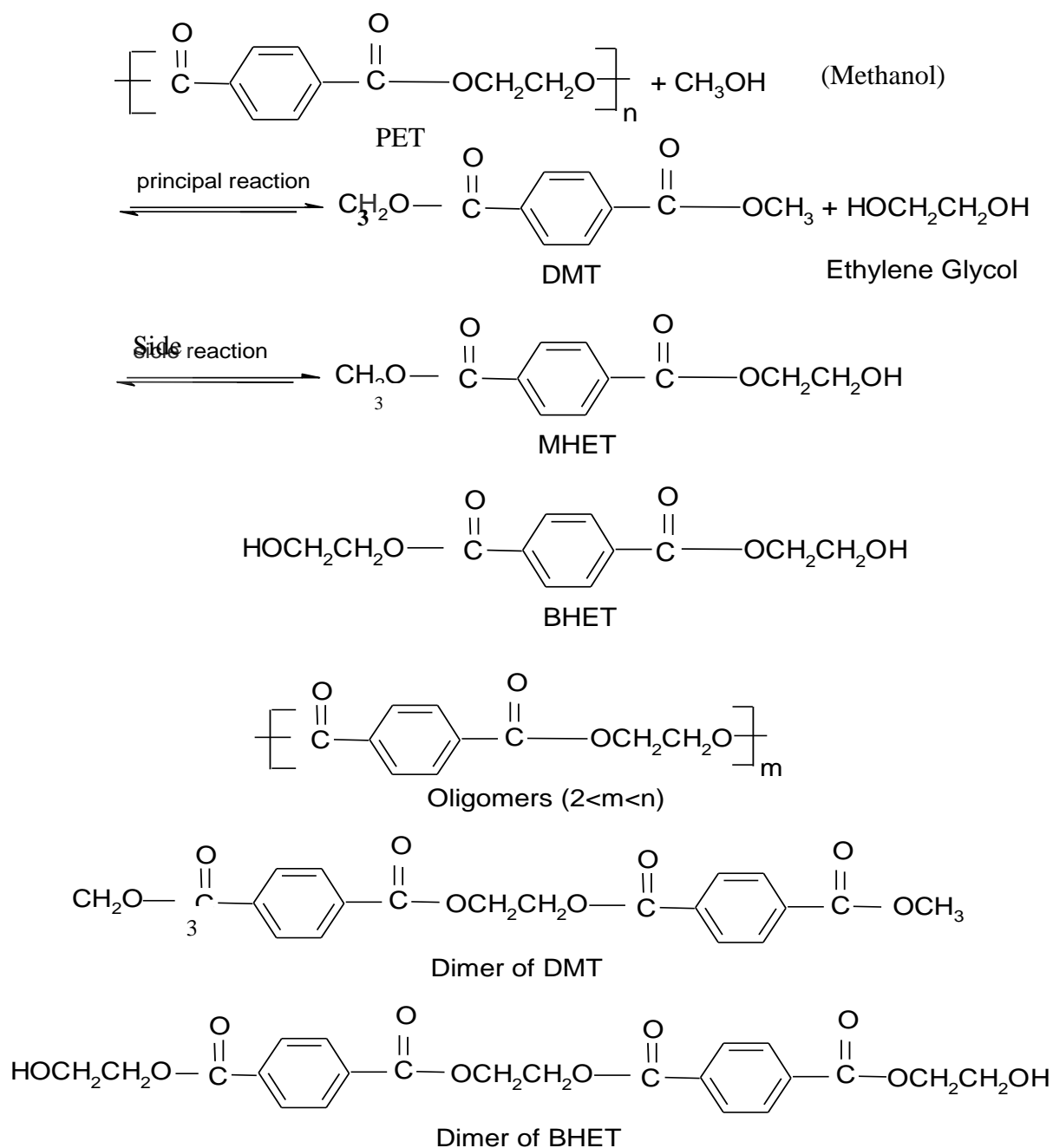
The initial weight for PET subjected to gamma rays is 0.5 g. was reduced to 0.48 .0.4, 0.31 and 0.29 g respectively at doses; 10, 20, 40 and 60 kGy. Figure 1 shows the decrease in PET weight with variation gamma absorbed dose.

Figure 2 shows the increasing in number of moles or separated particles from PET by increasing the dose rate during hydrolysis by gamma. This was calculated using total weight from PET which has a known molecular weight and the rest of PET (RPET) weight after each dose. Table 2 summarized he bands and the molecular weight for each product after irradiation.

1.2. Hydrolysis Products:

To study the influence of γ -ray on the depolymerization, the experiments were carried out at 11.0 MPa, 533 K at 10, 20, 40 and 60 kGy.

The yield of BHET dimer appears at Rt 3.5 at 10 kGy and at 20 kGy three elution bands BHET, MHET and DMT at Rt 1.9 , 2.28 and 4.06, respectively, ^(9, 22). Scheme (I) of depolymerization is clear as follows:

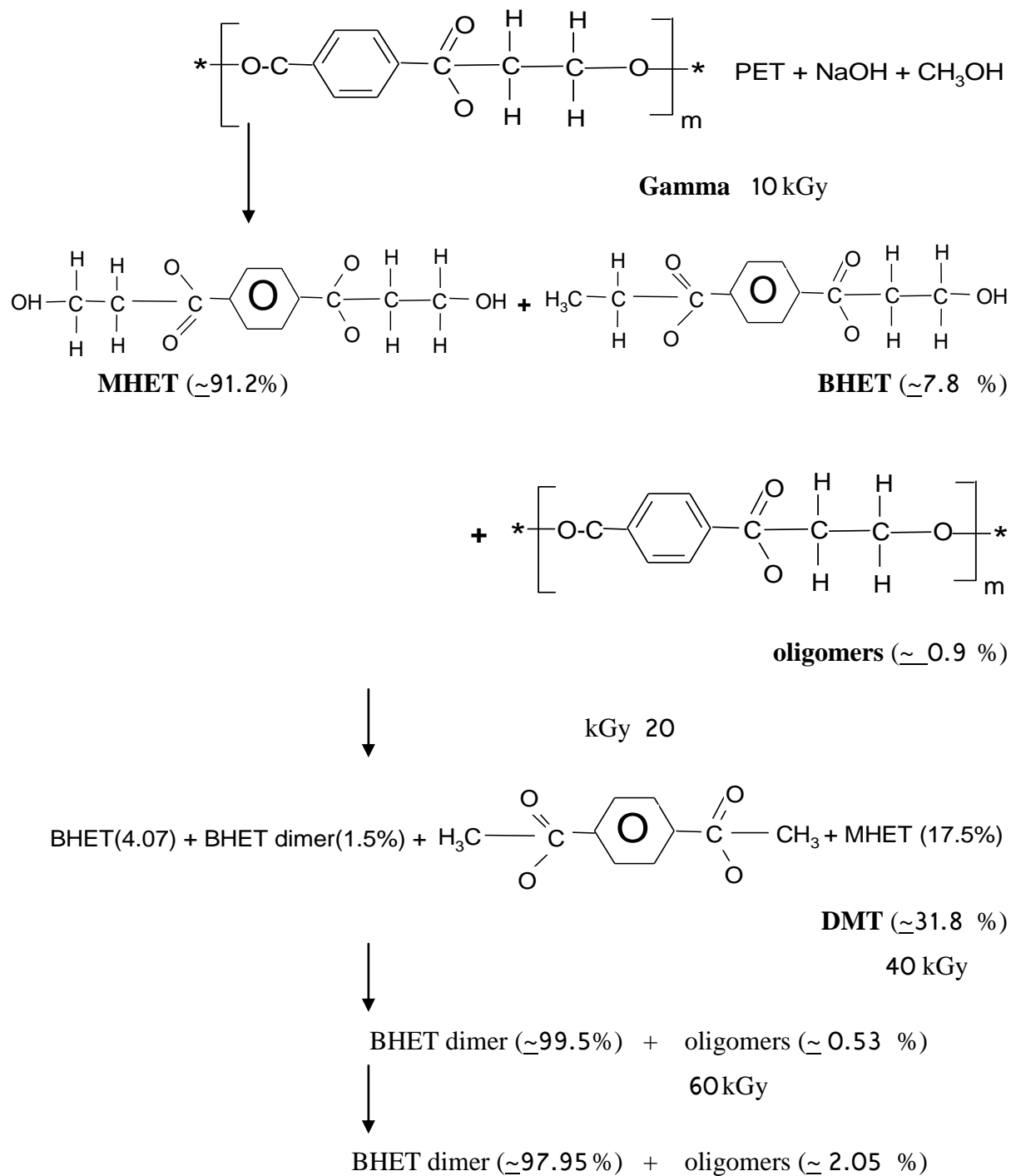


Scheme (I)

We suggest that depolymerization occurred at 10 kGy to dimer of BHET which separated from flaks surfaces and when the dose increase to 20 kGy this dimmers which represent 99.5 % of solution separated as BHET, represent 17.5 % and MHET 33.21 and DMT 31.79 % and small amount not detected (neglected to detect) from BHET dimer and oligomers.

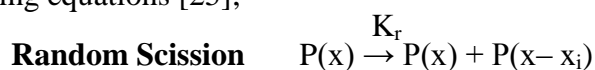
After 40 kGy BHET dimer was detected by HPLC with conc. 99.4 and at 60 kGy with conc. 97.95 may be due to increase of dose, the separated moles from the surface of PET increase, while at 20 kGy separated to MHET, BHET and DMT, this lasts product DMT separated moles at 20 kGy. Figures 3-6 shows the HPLC spectrum at different doses.

From the above mentioned data the structure of products after irradiation by γ -rays, may be represented as follows by Scheme (II);



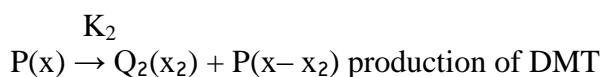
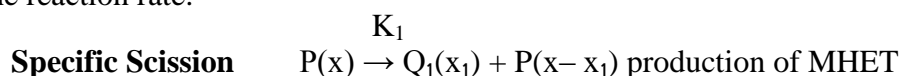
Scheme (II)

It is clear that the hydrolysis by gamma radiation at 10 kGy produces MHET as main products which detected with concentration of 91.2% and after 20 kGy decomposed to DMT with about 31.8% and the other products may be oligomer which is detected with a small amount in bands 6-8 [9]. BHET is polymerized after 20 kGy to 1.5 % BHET dimer by increasing the exposure dose. Increasing the dose absorbed leads to increase oligomers concentration from 0.53 to 2.05%. The PET degradation and the secondary reaction can be described in the following equations [25];



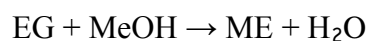
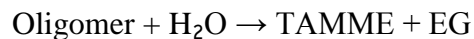
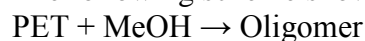
Where; $P(x)$ = polymer, $P(x-x_i)$; $i = 1, 2$.MW Ds of reaction mixture based on molecular function,

K_r = the reaction rate.



Where K_1, K_2 the rate of formation

The following scheme shows the different steps during hydrolysis occurred ⁽²⁵⁾



2. PET alkaline Hydrolysis (NaOH/CH₃OH) by reflux

2.1. Weight decrease in PET Flakes

The weight of PET reduced from 0.5 g to 0.39 g after 6 h with the particle size 0.6 mm, while for particle size, 0.3 mm PET the weight is reduced from 0.5 g to 0.0128 g after 6 h. As shown in Figures (7,8) unremarkable changes for the two particles sizes investigated by HPLC. The retention time (Rt) for the two spectra detected by HPLC is very enclose or equal to 4.13 min and 4.18 min. The yield of DMT which formed during the experiments also is similar agree to ⁽⁹⁾ and small amounts were detected by HPLC for oligomer with retention time (Rt) 7.34, Figure 7, undetected Oligomer shows in Figure 8.

DMT concentration after 3 h hydrolysis was found to be 98.6% and obtained after retention time of 4.42, Figure 9. After hydrolysis for 9 hours dimerization occurred to bring BHET dimer at Rt. 3.0 and undetected amount of DMT at Rt 4. 38 and oligomer at Rt. 7.05; Figure 10.

The products obtained from the solid PET hydrolysis using (NaOH/CH₃OH) by reflux mainly DMT and small amount of byproducts like MHET, BHET, dimer and oligomers. It can be assumed that alkaline methanolysis and methanolysis process have the same reaction mechanism in liquid NaOH and methanol ⁽²⁵⁾.

4. Conclusion

Gamma-rays can occur hydrolysis for PET easily using NaOH/MeOH and DMSO without exposure to any harmful emission comparing to reflux technique. Gamma-rays can be used for obtaining DMT with very low energy and time comparing to reflux method except that the yield of DMT by γ -rays is less than 50% while the time in gamma is half of reflux process. Alcoholysis also seems successful. Methanolysis and ethylene glycolysis are of particular interest because they can afford dimethyl terephthalate and di(hydroxyethyl) terephthalate which can also be used as starting monomers, respectively.

ACKNOWLEDGEMENT

The authors would like to thank greatly Prof. Dr. H.F. Aly for his encouragement and advice during this work and Prof. Salah Khalifa for help me in this paper.

References

- [1] Naima A. El-Gendy; Ph. D. Thesis, "Radiation and Photochemical Degradation of some Organic and Polymeric Materials in Wastewater", Institute of Environmental Studies and Research, Ain Shams Univ. Cairo, Egypt (2005).
- [2] D. Paszun and T. Szychaj; *Ind. Eng. Chem. Res.*; 36, 1373 (1997).
- [3] J. Scheirs; *Polymer Recycling*; 4, 119; (1998).
- [4] S.H. Mansour and N. E. Ikladious; *Polymer testing*; 21,497(2002).
- [5] O. Abdulrasoul and M. Alireza; *Polym. Intern.*; 35,728 (2004).
- [6] G. Xi., M. Lu. and S.Chen; *Polym. Degrad. Stab.*; 87, 117 (2005).
- [7] O. Sato, K. Arai and M. Shirai; *Catalysis Today*; 111, 297 (2006).
- [8] K. Hideki., O. Masa-aki., S. Kazuo and M. Hiroshi; *Polym. Degrad. Stab.*; 79, 529 (2003).
- [9] Y. Yang., Y. Lu, H. Xiang, Y. Xu and Y. Li; *Polym. Degrad. Stab.*; 75, 185 (2002).
- [10] G.M. de Carvalho, E.C. Muniz and A.F. Rubira; *Polym. Degrad. Stab.*; 91, 1326 (2006).
- [11] G. Grause, W. Kaminsky and G. Fahrback; *Polym. Degrad. Stab.*; 85, 571 (2004).
- [12] G. Güçlü, T. Yalçinyuva, S. Özgümüş and M. Oraby; *Polymer*; 44, 7609 (2003).
- [13] V. Kosmidis, D. Achilias and G. Karayannidis; *Macromol. Mater. Eng.*; 286, 10 (2001).
- [14] A. Bisio and M. Xanthos; "How to Manage Plastic", Hanser Gardner Cincinnati, OH. (1994).
- [15] J.R. Campanelli, M.R. Kamal and D.G. Cooper; *J. Appl. Polym. Sci.*; 54, 1731(1994).
- [16] S.C. Lee, Y.W. Sze and C.C. Lin; *J. Appl. Polym. Sci.*; 52, 867 (1994).
- [17] J. Brandrup, M. Bittner, G. Menges and W. Michaeli; "Hanser Gardner" Cincinnati, OH. Japan (1996).
- [18] J.Y. Chen, C.F. Ou, Y.C. Hu and C.C. Lin; *J. Appl. Polym. Sci.*; 42, 1501(1991).
- [19] P. Johnson and D.A. Teeters; *Am. Chem. Soc. Div. Polym. Chem.*; 32, 144 (1991).
- [20] S. Baliga and W.T. Wong; *J. Polym. Sci. Part A: Polym. Chem.*; 27, 2071 (1989).
- [21] A. Oku, L.C. Hu and E. Yamada; *J. Appl. Polym. Sci.*; 63, 595 (1997).
- [22] L.C. Hu, A. Oku, E. Yamada and K. Tomari; *J. Polym.*; 29, 708 (1997).
- [23] M. Ramsden and J. Phillips; *Chem. Tech. Biotechnol.*; 67, 131 (1996).
- [24] S. Mishra, A.S. Goje and V.S. Zope; *Poly. Reaction Eng.*; 11, 79 (2003)
- [25] M.Goto, H.Koyamoto, A.Kodama, T.Hirose, S.Nagaoka and B.J.McCoy; *AIChE J.*; 1,48(2002)

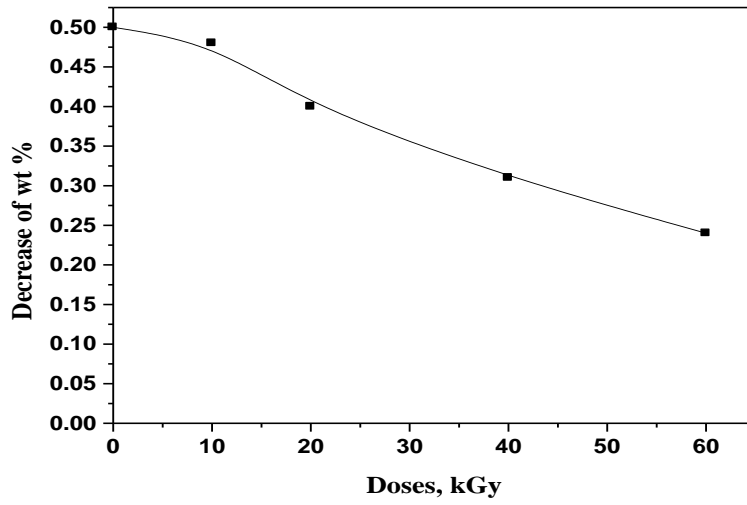


Fig.(1): Variation of PET weight decrease with increasing absorbed dose (kGy) by gamma radiation.

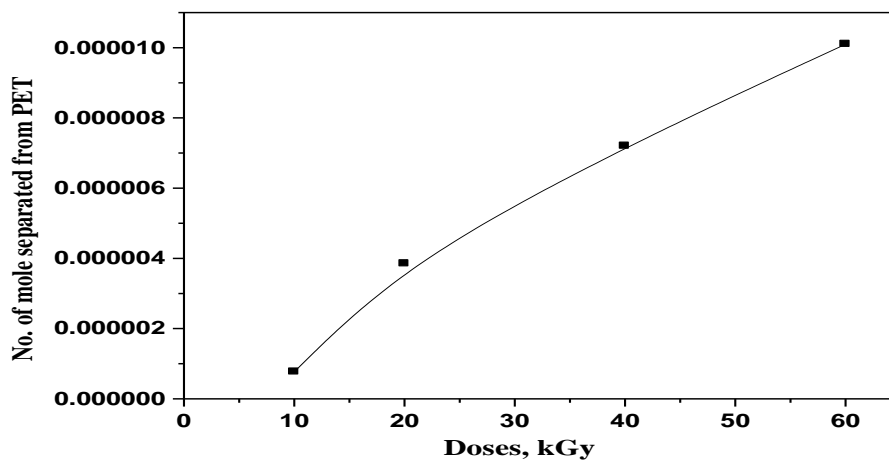


Fig.(2): Variation of RPET separated moles with increasing dose of gamma irradiation.

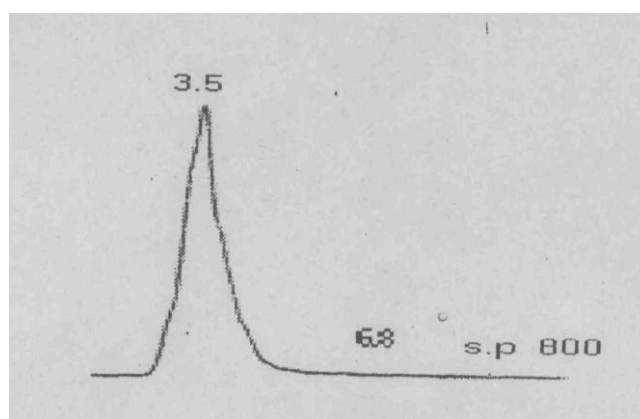


Figure 3: HPLC spectrum of the alkali-decomposition of PET by γ -irradiation dose of 10 kGy, Rt (3.5 min.) BHET dimer.

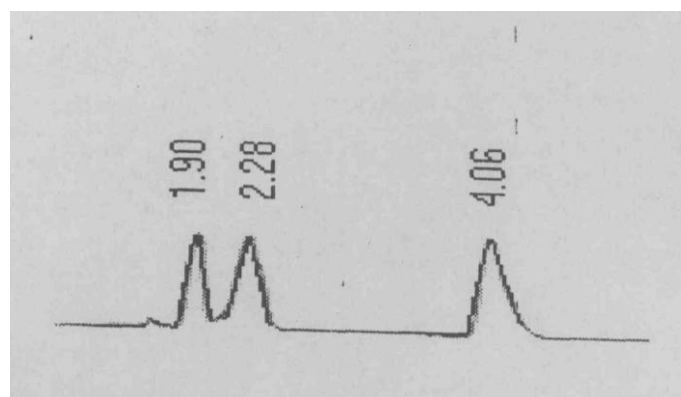


Figure 4: HPLC spectrum for the alkali-decomposition of PET by γ -irradiation dose of 20 kGy, Rt = (1.9 min) BHET, (2.28 min) MHET, (4.06 min) DMT.

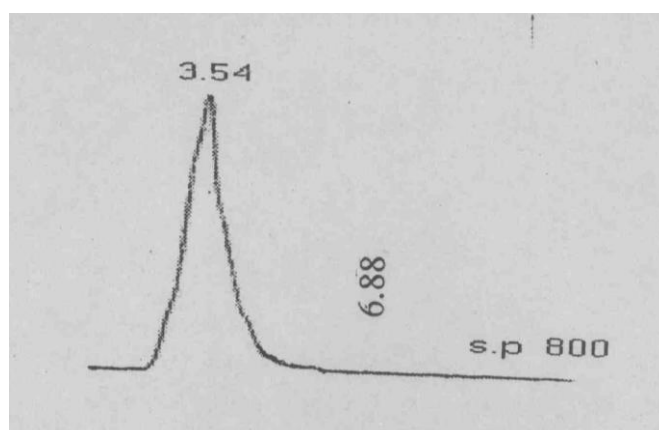


Figure 5: HPLC spectrum obtained from the alkali-decomposition of PET by γ -irradiation dose of 40 kGy, (Rt =3.54 min) BHET dimer.

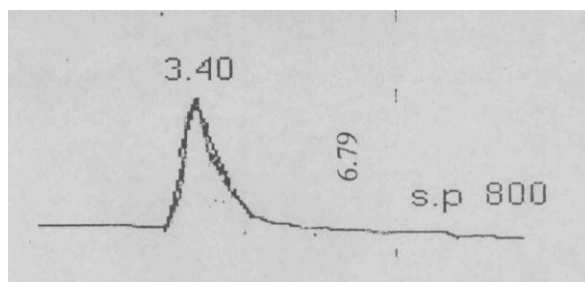


Figure 6: HPLC spectrum of the alkali-decomposition of PET by γ -irradiation dose of 60 kGy, (Rt = 3.4 min) HBET dimer.

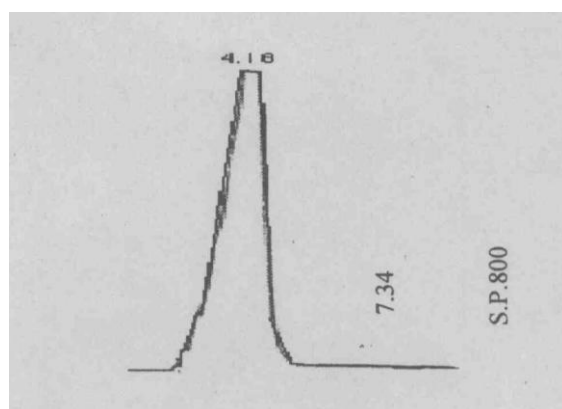


Figure 7: HPLC spectrum obtained from the alkali-decomposition of PET of particle size 0.3 mm by reflux (Rt = 4.18 min) DMT.

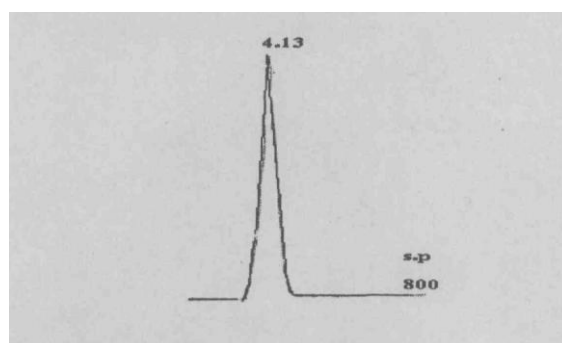


Figure 8: HPLC spectrum obtained from the alkali-decomposition of PET of particle size 0.6 mm by reflux (Rt = 4.13 min) DMT.

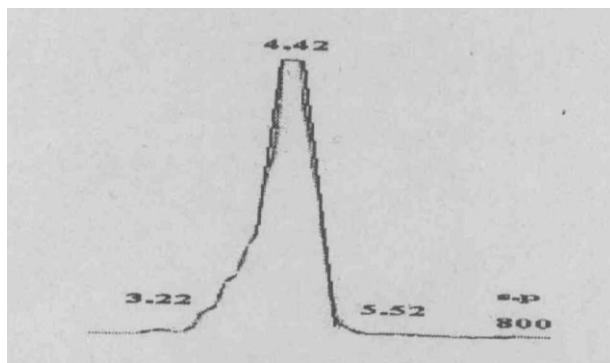


Figure 9: HPLC spectrum obtained from the alkali-decomposition of PET of particle size 0.6 mm by reflux after 3 h (Rt = 4.42 min) DMT.

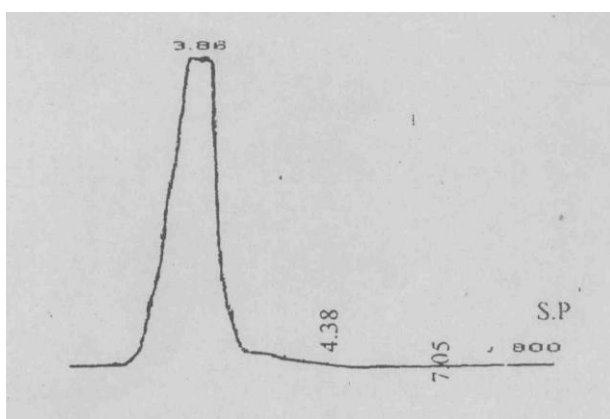


Figure 10: HPLC spectrum obtained from the alkali-decomposition of PET of particle size 0.6 mm by reflux after 9 h (Rt = 3.86 min) BHET dimer.

Table 1: The solubility parameter for certain solvents.

Materials	Material solubility parameter, $\delta(\text{Jm}^{-3})^{1/2}$
PET	21.6
DMSO	24.6
Ethylene glycol	29.9
Ethanol	26
Water	41.9

Table 2: Products and byproducts evaluated by HPLC after PET irradiated its structure and molecular weight for each component.⁽⁹⁾

Band at retention time (Rt) (min)	Product	Structure	MW
1	BHET Bis(hydroxy 1 terphthalate		425
2	MHET Methyl hydroxyl terphthalate		382
3	BHET dimer		644
4	DMT		222
5	DMT dimer		414
6-8	oligomers		(2<m <n)

Table 3: Shows the product and byproduct after irradiation doses for PET evaluated by HPLC; the structure and molecular weight (MW) for each evaluated component.

retention time Rt (min)	Byproducts	Product	Concentration, %	Dose rate kGy/h
3.5	BHET		99.47	10
4.06		DMT	31.796	20
2.28	MHET		33.21	20
1.9	BHET		17.5	20
3.54	BHET dimer		99.46	40
3.4	BHET dimer		97.95	60

**Military Technical College
Kobry El-Kobbah,
Cairo, Egypt**



**5th International Conference
on
Chemical & Environmental
Engineering
25 - 27 May, 2010.**