Web of Technology: Multidimensional Research Journal
webofjournals.com/index.php/4

INFLUENCE OF CONDITIONS FOR ALCOHOLYSIS OF SECONDARY POLYETHYLENE TEREPHTHALATE ON THE OUTPUT OF BIS(HYDROXYETHYL) TEREPHTHALATE

Abduvohidov I.Q., PhD
Senior Lecturer, Department of Fundamentals of Medical Chemistry
Andijan State Medical Institute, Ministry of Health of the Republic of Uzbekistan
E-mail: abduvohidoviqbol572@mail.com
ORCID iD: 0009-0009-7431-556X

No’monov A. N.
Student at Andijan Presidential School 170100,
Uzbekistan, Andijan, Alisher Navoiy shox St., Building 73
E-mail: numonovabdulloh09@gmail.com
ORCID iD: 0009-0009-7431-556X

Abstract

This study presents the results of alcoholysis of secondary polyethylene terephthalate (PET) using ethylene glycol (EG). The main focus is to identify the optimal conditions for the formation of bis(hydroxyethyl) terephthalate (BHET), an important intermediate in PET production. The effects of alcoholysis duration, catalyst type, and catalyst amount on BHET yield were studied using a PET:EG molar ratio of 1:4. By varying the alcoholysis duration from 8 to 10 hours and adjusting the type and quantity of catalyst (zinc acetate and titanium tetrabutoxide), the BHET yield was increased from 64.4% to 70.1%. Key physicochemical parameters of BHET were obtained and found to be consistent with data from other researchers.

Keywords: Secondary polyethylene terephthalate, ethylene glycol, bis(hydroxyethyl) terephthalate, alcoholysis, fraction, yield increase, productivity, physicochemical parameters.

Introduction

Since 1970, PET has become one of the most widely produced polymers. In 2015, global PET production reached 70 million tons: 49.3 million tons were used for fibers and yarns, and 20.6 million tons for packaging bottles. According to the 23rd PCI Consulting Group (Europe), PET’s global market size was $36.13 billion in 2015 and is projected to reach $65.4 billion by 2022, with annual growth of 8–9%. This implies a parallel increase in PET waste generation. In Uzbekistan alone, 82,000 tons of PET bottles were consumed in 2022, leading to equivalent PET waste. Known recycling methods for secondary PET (IPET) include physical recycling (into fibers, yarns, and household goods) and chemical hydrolysis to recover terephthalic acid or polyether polyols containing hydroxyl groups. Unsaturated polyesters and alkyd resins have also been synthesized. Recently, research into BHET production from IPET has significantly expanded.

Based on these developments, we conducted a study on how alcoholysis conditions affect the yield of bis(hydroxyethyl) terephthalate.

Materials and Methods

Raw materials: Ethylene glycol (Russia) was purified via vacuum distillation at 110–115 °C under residual pressure of 0.90–0.97 kgf/cm². The product had a refractive index of nD = 1.4338 to 1.4345. Secondary PET came from used beverage bottles (melting point: 240–250 °C; density: 1.284–1.296 g/cm³). Zinc acetate was used as per GOST 5823-78.

Synthesis of BHET: Following the method described in [14], alcoholysis was performed in a four-necked flask equipped with a mixer, thermometer, and nitrogen inlet. Dried PET particles (48 g) and EG (62.18 g) were used at a 1:4 molar ratio (PET:EG). Nitrogen was passed continuously, temperature was raised gradually to 100 °C, and then to 196 °C over 60 minutes. Alcoholysis was conducted for 3–8 hours. Afterward, the mixture was cooled to 100 °C and distilled water (1:4 ratio) was added, stirred at 90–95 °C for 30 minutes, and filtered (Fraction 1). The filtrate was cooled to −2 °C to precipitate white crystals, which were then filtered (Fraction 2). Products were vacuum-dried at 60–65 °C under 50–60 mm Hg. Ethylene glycol was recovered by vacuum distillation; oligomers remained in the flask.

Analytical Methods:

Hydroxyl group content was measured per GOST 25261-82; melting point and molecular weight per [15] and [16]. IR spectra were recorded using PerkinElmer and Specord-75UR instruments.

Results and Discussion

Alcoholysis is a process of chemical destruction of secondary polyethylene terephthalate in the presence of alcohols of various functional and natural origin. Using the example of alcoholysis of IPET with ethylene glycol [14], it was shown that the final product is bis(hydroxyethylene) terephthalate (BGTF) and oligomers of various molecular weights. It should be noted that for the technologies used in the bottle industry, the synthesis of primary polyethylene terephthalate from alcoholysis products is the target, which leads to a decrease in the cost of primary polyethylene terephthalate (PET). The above determines the need to conduct studies to identify opportunities for increasing the yield of BGTF. The results of fractionation of the 8-hour alcoholysis product are presented in Table 1.

1-Table Material balance of alcoholysis product of secondary polyethylene terephthalate with ethylene glycol
(Alcoholysis conditions: RPET:EG ratio = 1:4 mol e unit/mol; temperature 190°C and duration 8 hours.)

Input				All	Output										All
BGTF		EG			1-fraction		2- fraction		3- fraction		Ethylene glycol		Cubic		
g	%	g	%		g	%	g	%	g	%	g	%	g	%	
48	43,56	62,18	56,43	110,18	14,7	13,34	38.03	34,52	4,95	4,5	33,89	30,76	18,05	16,39	110,18

As can be seen from the data in Table 1, fraction 1 was 13.34%. Fraction 2 was 34.29%, fraction 3 was 4.5%. The yield of free monomer was ethylene glycol 30.76%, and the residual VAT was 16.39%.

These data show that fraction 1 differs significantly from similar values of fraction 2 in terms of melting point. It should be noted that fractions 2 and 3 have very close melting points and molecular weights of 112 ° C, 281 and 111 ° C, 242, respectively, which allows them to be combined into one fraction.

The DSC curves of the combined second and third fractions (Fig. 1) have an endo peak at 110.15 ° C. The molecular weight of this fraction, determined by cryoscopy, is 254-256. According to literature data (DSC analysis results), the onset and end temperatures of BGTF melting are characterized by 106 and 109oC, respectively [14].

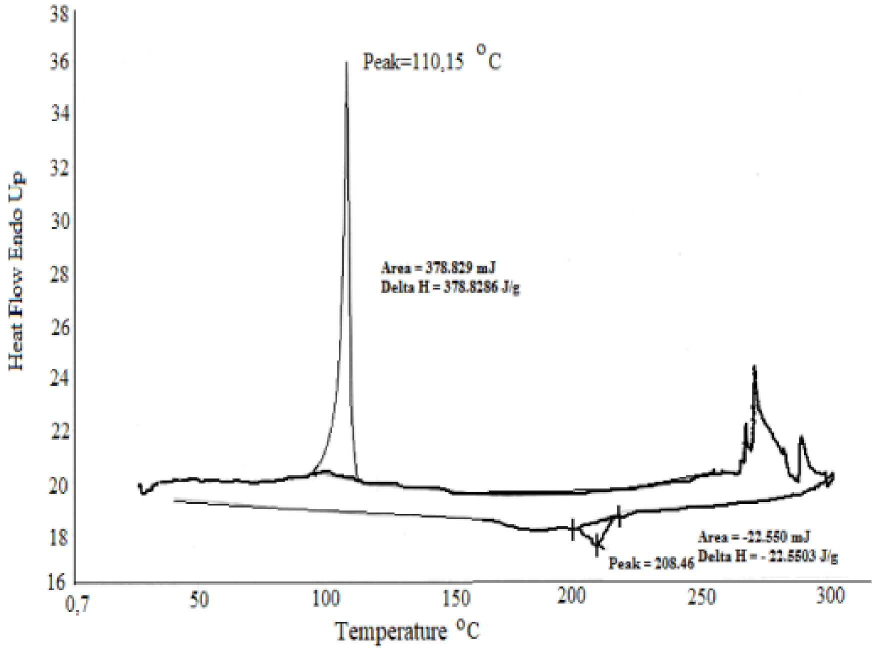

Fig.1 - DSC analysis of the obtained BGTF

Theoretical calculation of the molecular weight based on the BGTF formula gives a value of 255.

The calculated value is very close to the molecular weight values of the second and third fractions.

The physicochemical properties of the vacuum-dried fractions are presented in Table 2.

2-table Physicochemical properties of fractions isolated from IPET alcoholysis products obtained by alcoholysis for 8 hours.

№	Name	Melting point, ºC	Molecular mass
1.	Fraction №1	164	580,5
2.	Fraction №2	112	281
3.	Fraction №3	111	242
4.	2-3- fractions	110,15	254-256

According to the literature [14], during alcoholysis of IPET with ethylene glycol in a ratio of 1: 4 mol/mol, the melting points of fraction 1 = 170 ° C, fraction 2 = 106 ° C and fraction 3 = 109 ° C and dimer = 174 ° C are formed bis (2-hydroxyethylene) terephthalate and dimer, molecular mass 254-256 g / mol. In this regard, fractions 2 and 3 can be called bishydroxyethyl terephthalate. The yield of the main product, BGTF, was 64.4%, and the dimer was trimers.

a Fraction 1-2 b) Fraction 3

Fig. 2- Fractions of IPET alcoholysis products

Therefore, it can be concluded that the second and third fractions are BGTF. If after 8 hours of alcoholysis of IPET with ethylene glycol, the yield of BGTF was 64.4%, then increasing the duration of alcoholysis to 10 hours and increasing the concentration of zinc acetate catalyst to 1%, the yield increases to 67.5%.

Another way to increase the yield of BGTF is to change the catalyst. Thus, carrying out the reaction of IPET and EG in the presence of 0.5% of the catalyst tetrabutoxytitanium showed that if the duration of alcoholysis was 8 hours, if the yield of BGTF was 67.6%, then increasing the duration of alcoholysis to 10 hours leads to an increase in the yield of BGTF to 70.1 (Table 3).

Table 3 Effect of synthesis conditions on BGTF yield and properties

Duration of alcoholysis (hours)	Amount of catalyst (Zinc Asetate) %	Physico-chemical properties						Amount of cubic residue, %	Yield of BHET, %
		Avarage molecular mass			Melting point, °C				
		1-fraction	2-fraction	3-fraction	1-fraction	2-fraction	3-fraction		
8	0,5	580	280	225	164	112	110	7,26	64,4
10	0,5	893	261	232	164	112	109	5,48	67,5
10	0,7	730	250	236	164	111	110	5,91	67,5
10	1,0	780	253	228	169	109.5	108	5,93	67,5
	Amount of catalyst (Tetrabutoxytitanium) %								
8	0,5	731	240		166	110		4,48	67,6
10	0,5	745	245		165	112		4,71	70,0
10	0,5				168-170	108-110		4,61	70,1

It should be noted that when using tetrabutoxytitanium, a modification was made to the BGTF purification procedure, i.e., after separation of fraction 1, the filtrate was concentrated under vacuum by distillation of 70% of the water.

The solution was then kept at 0 - 2 ° C for a day. At the same time, the second and third fractions precipitated simultaneously. Thus, the effect of the conditions for the alcoholysis of secondary polyethylene terephthalate with ethylene glycol was studied. A modified technique was developed for the separation of bis(hydroxyethyl) terephthalate. Note: The original document includes graphs and spectral images such as DSC analysis and IR spectra. Due to the format limitations, these figures have not been embedded here but are described in the discussion sections.

References

1. Masardi N., G.S.I. PET market Overviev. CREON, Moskva. Available at: http://arpet.ru/material/4824. (accessed 18.02.2015).
2. Angel B. Polyester Fibres. The 23RD PCI Consulting Group European Polyester Industry Conference, 3 October, Berlin. Available at: https://www.plastics.ru/pdf/journal/2015/12/PET.pdf. (01.02.2016).
3. Adina Cata, Marinela Miclau, Ioana Ienascu, Daniel Ursu, Cristian Tanasie and Mariana N.Stefanut. Chemical recycling of polythelene terephthalate (PET) waste using sub- and supercritical water // Rev.Roum.Chim., 2015, – №60(5-6). – P. 579-585.
4. Пат. 2263658 Россия МПК7 С 07С51/9, В29 В17/02 Милан, Ирошек Ярославл. Способ химической реутилизации отработанного полиэтилентерефталата: №2002 126 254/04; заявл. 08,03.2001; Опубл. 10,11.2005.

5. Lopez-Forseca R., Ganzales-Marcos M.P., Gonzales-Velasoc J.R., Gutierrez Ortiz J.I. A kinetic study of the depolymerization of poly(ethylene terephthalane) be phase transfer catalysed alkaline hydrolysis // J. Chem. Technol and Biotechnol. 2009. 84, – №1. – P. 92-99.
6. Mancini C.D. Noqueira A.R., Rahgel E.C. Da Cruz N.C. Solid-state hydrolysis of postconsumer polyethylene terephthalate after plasma treatment // J. Appl. Polym. Sci. 2013. 127, – №3. – P. 1989-1996.
7. Пат. 176615 Польша, МПК^6 C 08 G 63/91, C 08 G 63/46. Sposob wytwarzania poliestroli // Ostrysz Ryszard, Penczek Piotr, Nazitjhlo .lulianna. – 303219; заявл. 27.04.94; Опубл. 30.7.99.
8. Sunain Katoch. Kinetics study of Unsaturated Polyester synthesized from waste PET // Asian Journal of advanced basis sciences. 2013. – №1.– P. 87-92.
9. A.B. Juraev, R.I. Adilov, T.A. Nizomov, M.G. Alimuxamedov, F.A. Magrupov, Synthesis and Research of unsaturated Polyethers on the Basis of Secondry Polyethyline Terephthalate // Kautschuk Gummi Kunststoffe, 2014, – №4. – P. 41-44.
10. Костенко И.Н., Чеников И.В. Модификация алкидов вторичным полиэтилентерефталатом // Лакокрасочные материалы и их применение, 2010, – №4. – С. 42-45.
11. 11.Пат RU 2285705. МКИ C08J 11/04. Способ получения алкидных олигомеров и алкидный лак, содержащий алкидный олигомер // Цейтлин Г.М. и др. Заяв. 2005117785/04. Опубл. 20.10.2006 Бюл. № 29.
12. Chen F., Wang G., Shi C., Zhang Y., Zhang L., Li W., Yang F. Kinetics of glycolysis of poly(ethylene terephthalate) under microwave irradiation // J. Appl. Polym Sci. 2013. 127, – №4. – P. 2809-2815.
13. Joshi Sapna. Study on Depolymerization of Waste PET scrap (Polyethylane terephthalate) in to monomer of bis(2-hydroxyethyl terephthalate) // Institute of technology, Nirma University, 08-10 desember, 2011. – P.1-2.
14. Baliga Satish, Wongwing T. Depolymerization of PET retsirkulizirovannogo from used plastic bottles for drinks // J.Polym.Sci.A. -1989, -27, – №6, – P. 2071-2082.
15. Махсудов Й.И. Polimermateriallarini sinashga oid praktikum [Practice of testing polymer materials]. Toshkent, Teacher Publ., 1884. 196 p.
16. Кабанова В.А. Практикум по высокомолекуляным соединениям [Workshop on high-molecular compounds]. Moscow, Khimiya Publ., 1985, 224 p.