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Preparation and Characterization of Diols and Polyols Based on Aminolysis of Poly (ethylene terephthalate) Wastes with Alkanolamines

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Abstract

The Plastic Waste phenomenon, which is the result of increasing poly (ethylene terephthalate) production and the wide range PET consumption in different industries, caused one of the major environmental concerns. Therefore,many different ways have been studied and applied for chemical recycling of PET. One of the most important ways to depolymerize poly (ethylene terephthalate) is the aminolysis procedure. In the present study, PET aminolysis reactions have been done in order to optimizethe usage of polyester wastes.The compound of polyol obtained from aminolysis reactions could be an alternative of polyols used in common synthesizes of polymeric materials in order to produce new industrial polyesters and polymers with noble features.The products then was characterized by the use of analyzing tests such as hydroxyl value determination and total nitrogen measurement based on ASTM standards and systematic analysis by FTIR, ^{1}H NMR, elemental analysis and differential scanning calorimetric (DSC).

Keywords: *Plastic waste phenomenon , Aminolysis, Chemical recycling, Alkanolamines.*

Introduction

PET is a polymer with a long saturated chain. PET bottles have characterized by high resistant, low weight, low permeability of gases (mainly CO_2) as well as aesthetic appearance (good light transmittance, and smooth surface). One of the most important features of PET, decisive in the choice of its wide application in the manufacture of packaging for the food industry, is that it doesn’t have any adverse side effect on the human body [1].

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The increasing poly (ethylene terephthalate) production in line with a wide range of usage in different industries caused the plastic waste bulk phenomenon. Aminolysis is one of the most important procedures of poly (ethylene terephthalate) chemical recycling. A PET aminolysis reaction which is the effect of amine on PET polymer chain in the presence of transesterification catalysts, then, break the ester chain, and formed the terminal groups of NH/ OH on molecules.

Aminolysis process has seldom used for PET chemical recycling, at least for deep polymer degradation. The superficial partial aminolytic degradation of PET fibers has been the subject of numerous research studies [2-5], and is currently applying an industrial scale. Apparently, the progress of aminolysis process of PET fibers with a primary aqueous solution [5] has been more than when it was in the gas form [6]. In most reports, this method has been used amines such as ethanolamine [7-9], triethyamie [10], butylamine [7,11], and tetraamine[10].

Depolymerization of the PET waste using different amine, such as allylamine [12], morpholine and hydrazine [13] and polyamins [14] has studied in the polish laboratories. PET waste when treated for 2 h with an excess of allylamine at 170 °C under pressure of 2 MPa gave the product N, N'-basally terephthalamide. The product with high melting point of 217 to 219 °C may be considered as a high temperature solid cross linking agent for unsaturated polyester compositions. The reaction was usually carried out using primary amine aqueous solution, most frequently methylamine[7,11,15,16], ethylamine[11,15,16], and ethanolamine[11] in the temperature range of 20-100 °C.

Anhydrous n-butylamine was also applied as an aminolytic agent at a temperature 21°C [11]. Simple chemicals like glacial acetic acid or simple salts which are found to be capable of depolymerising of PET fiber waste through aminolysis was studied by Shakla and Harad [2].In this process, the yield and purity of the chemically reactive product BHETA are high order with much less reaction time. The product of depolymerization has the great potential of recycling it into useful products through various chemical reactions. Aminolization of poly (ethylene terephthalate) with ethanolamine in the molar ratio of 1:6 (PET: monoethanolamine) under reflux in the presence of different catalysts namely as glacial acetic acid, sodium acetate, and potassium sulfate in 8h has been studied. At the end of the reaction, distilled water was added to the reaction mixture with vigorous agitation to precipitate out product, bis(2-hydroxyethyl terephthalamide (BHETA) [2].

Zahn and Pfeifer [13] carried out aminolysis of PET with a solution of hydrazine, benzyl amine, ethylene diamine, hexamethylendiamine, piperidine, and aniline. They obtained different reaction products as the diamines as of terephthalic acid, which do not possess any potential for further chemical reaction. So far, aminolysis PET recycling method was used less than other PET chemical recycling methods such as glycolysis and hydrolysis [17-19].

In this research, to reach the optimal conditions to obtain the monomer units in the aminolysis of PET with alkanolamines (monoethanolamine, diethanolamine, and triethanolamine), many reactions were operated and different factors, such as the time, the alkanolamines types and the ratio of alkanolamines to PET were evaluated. The usage of the reaction products as polyol compounds for the synthesis of other polymers in commercial scale is being studied.

Experimental

Materials

Materials used for PET aminolysis are as follows: PET chips with an average size of 0.5×0.5 cm, monoethanolamine (MEA), diethanolamine (DEA), and triethanolamine (TEA)(Arak Petrochemical Co., Iran).Other the chemicals and solvents were obtained from E-Merck (Darmstadt, Germany).

Instruments

Digital Kjeldahl (Foss 2300), Elemental Analysis (Elementor Analysem system GmbH Vario EL III), Nuclear Magnetic Resonance (^{1}H NMR) (BRUKER AVANCE 400 [400 MHz]), Infrared spectrum was recorded by BRUKER IR spectrophotometer (TENSOR 27) and Differential Scanning Calorimetric (DSC) (NETZSCH 200F3).All reactions were conducted under a nitrogen atmosphere.

PET Aminolysis

PET Aminolysis by Monoethanolamine

Poly (ethylene terephthalate) was reacted with MEA in different molar ratios of 3:1 and 6:1. The sodium acetate 1.0% w/w was added as a catalyst (by weight of the polymer) in a 4-neck round-bottom flask equipped with mechanical stirrer with an average speed of 250 rpm, thermometer, and condenser under a nitrogen atmosphere. Each reaction performed separately for 5 and 8 hours at 160-190 ˚C.

At the end of the reaction, distilled water was added in excess to the reaction mixture with vigorous agitation to precipitate out the product, bis (2-hydroxy ethyl) terephthalamide (BHETA). The precipitate obtained was filtered and dissolved in distilled water by boiling for about 30 min. White crystalline powder of BHETA was obtained by first concentrating the filtrate by boiling and then chilling it. It was further purified by recrystallization in water. The white precipitate obtained was separated from residues by filtering and washing with water then dried in oven at 80 ˚C and weighted. Obtained products were named as AM1-AM4. Table 1 shows conditions in which aminolysis reactions and reaction mass yield were performed. The reaction of PET aminolysis with MEA is illustrated in Figure 1.

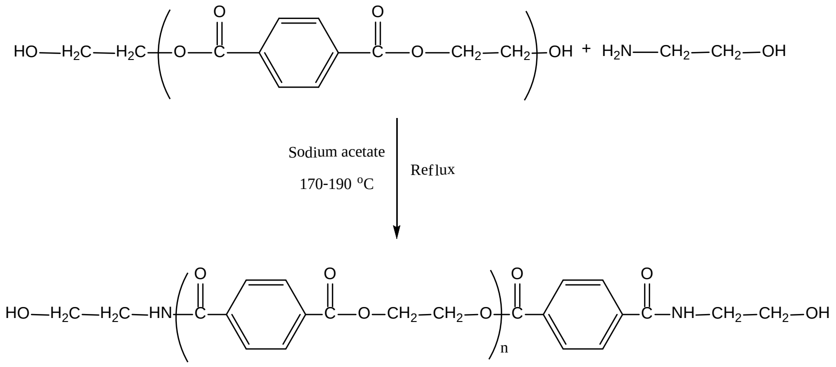

Figure 1. Aminolysis of Poly (ethylene terephthalate) by Monoethanolamine.

PET Aminolysis by Diethanolamine and Triethanolamine

Poly (ethylene terephthalate) was reacted with DEA (DEA: PET) and TEA (TEA: PET) with 2 M ratios 3:1 and 6:1 in the presence of sodium acetate 1.0% w/w (by weight of the polymer) in a 4-neck round-bottom flask equipped with mechanical stirrer with an average speed of 250 rpm, thermometer and condenser under a nitrogen atmosphere. Each reaction performed separately for 5 and 8 hours at 160-190 °C.

Table 1. Conditions of Performed Aminolysis Reactions and Reaction Mass Yield.

Product name	Mass Yield (%)	Mole ratio (g/mol)	Reactant	Test number	Reaction time
AM-1	112	1:3	PET: MEA	1	5 hours
AM-2	125	1:6	PET: MEA	2	
AD-1	123	1:3	PET: DEA	3	
AD-2	135	1:6	PET: DEA	4	
AT-1	132	1:3	PET: TEA	5	
AT-2	143	1:6	PET: TEA	6	
AM-3	118	1:3	PET: MEA	7	8 hours
AM-4	131	1:6	PET: MEA	8	
AD-3	100	1:3	PET: DEA	9	
AD-4	102	1:6	PET: DEA	10	
AT-3	108	1:3	PET: TEA	11	
AT-4	110	1:6	PET: TEA	12	

At the end of the reaction, the mixture was dissolved in ethanol and no reacted PET was obtained after filtration. Then, ethyl acetate was added to the reaction mixture with vigorous agitation to precipitate out the product. The precipitate obtained from the reaction was filtered and dried at 80°C in oven. Obtained products were named as AD1-AD4 and AT1-AT-4. Table 1 shows the conditions in which the aminolysis reactions and reaction mass yield were performed. PET aminolysis reaction with DEA and TEA were shown in Figures 2 and 3.

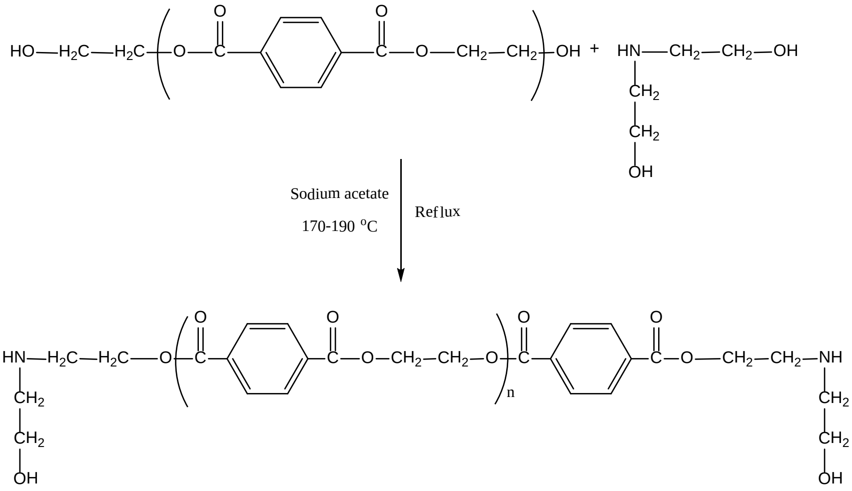

Figure 2. Aminolysis of Poly (ethylene terephthalate) by Diethanolamine.

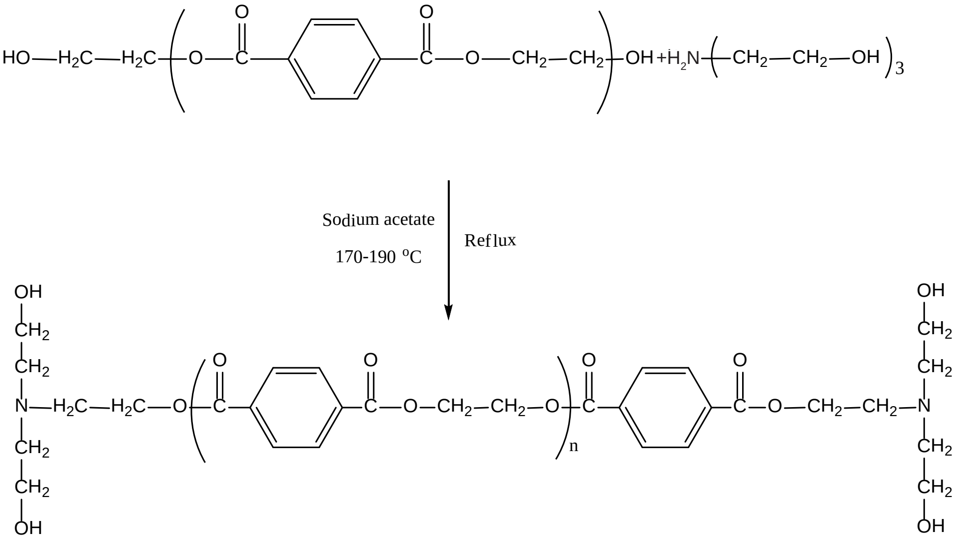

Figure 3. Aminolysis of Poly (ethylene terephthalate) by Triethanolamine.

Results

Structural and chemical features of products were analyzed based on different laboratory tests. The value of hydroxyl was determined based on standard methods [20] and total nitrogen was measured at the base of standard procedure [21]. In addition, total nitrogen accounted from standard procedure was compared with total nitrogen obtained from Digital Kjeldahl, and Elemental Analysis of products was carried out, randomly. The hydroxyl value determination, average molecular weight, and whole nitrogen value data was shown in Tables 2 and 3.

Table 2. Hydroxyl Value (HV) and Number Average Molecular Weight ($\overline{Mn}$), for Different Oligoesters.

Mn(g/mol)*	Hydroxyl Value			Product Name
	OHV [17]	B (ml)	A (ml)	
476	235.6	34.6	30.4	AM-1
339	330.9	55.1	49.2	AM-2
400	280.5	55.1	50.1	AM-3
318	353.4	55.1	48.8	AM-4
645	173.9	38.6	35.5	AD-1
500	224.4	38.6	34.6	AD-2
540	270.6	38.6	34.9	AD-3
364	308.5	38.6	33.1	AD-4
783	280.5	53.2	48.2	AT-1
656	342.2	53.2	47.1	AT-2
690	325.4	53.2	47.4	AT-3
588	381.5	53.2	46.4	AT-4

*Based on Equation 1

Table 3. Achieved Results from Total Nitrogen Analysis.

Total Nitrogen						Product Name
Theoretical			Elemental Analysis	Digital Kjeldahl	ASTM D 1013-88	
n=2	n=1	n=0				
4.40	6.30	11.10	10.88	10.88	10.51	AM-1
			-	-	10.61	AM-2
			10.92	10.92	10.79	AM-3
			-	-	10.91	AM-4
3.87	5.26	8.23	7.39	7.55	7.09	AD-1
			-	-	7.35	AD-2
			7.75	7.59	7.31	AD-3
			-	-	8.21	AD-4
3.45	4.51	6.54	5.39	5.41	5.32	AT-1
			-	-	5.63	AT-2
			4.51	4.54	4.59	AT-3
			-	-	4.91	AT-4

The detailed data from an IR spectrograph of PET sheet and the purified compound have shown in Table 4.

Table 4. The IR Spectrograph Data from PET and Products.

Compounds Name	**IR Spectrograph Data**
PET Sheet	In the spectrograph of PET sheet peaks corresponding to the primary alcohol, secondary amide, and amine have not been observed.
AM1-AM4	Primary alcohol: Peaks at 1051 and 3282 cm^{-1} Secondary amide stretching: Peaks at 1318, 1553 and 3357 cm^{-1} Stretching C-N: Peak at 1073 cm^{-1}
AD1-AD4	Primary alcohol: Peaks at 1039 and 3052 cm^{-1} Secondary amine stretching and bending: Peaks at 3334 and 1550 cm^{-1} Stretching C-N: Peak at 1070 cm^{-1}
AT1-AT4	Primary alcohol: Peaks at 1031 and 3098 cm^{-1} Stretching C-N: Peak at 1066 cm^{-1}

The products were dissolved in dimethyl sulfoxide (DMSO) and characterized by Nuclear Magnetic Resonance (^1H NMR). The monoethanolamine, peaks observed at 8.52 corresponding to –NHCO- groups, 3.28-3.51 corresponding to aliphatic CH_2-CH_2 proton, 7.93 corresponding to aromatic ring protons, and 4.72 corresponding to –OH groups. In ^1H NMR spectrums of obtained products by diethanolamine and triethanolamine reactions peaks in 3.45, and 3.47 show -OH groups, respectively. In the spectrum of diethanolamine product 3.41 relates to -NH- groups.

Melting and distortion point of obtained products reacted by monoethanolamine, diethanolamine, and triethanolamine recorded by Differential Scanning Calorimetric (DSC). Samples were introduced in aluminum pans hermetically closed and then introduced in the calorimeter. The DSC calibrated with standard Indium. 10 mg samples were heated from 25 to 400°C and the thermograms were recorded at a heating rate of 10 °C/min under dry nitrogen atmosphere. DSC graphs and analysis results are shown in Figure 4 and Table 5, respectively.

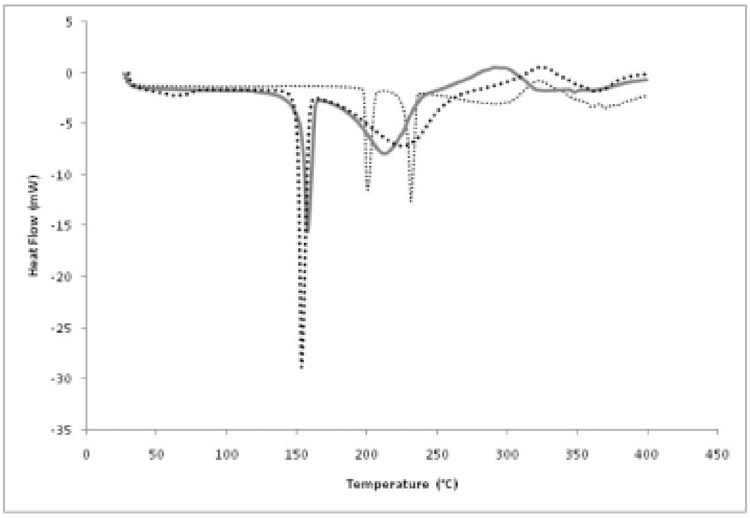

Figure 4. Differential Scanning Calorimetric (DSC) of Oligoesters Obtained of Aminolysis by (….) monoethanolamine, (__) diethanolamine, and (**…..**) triethanolamine.

Table 5. Melting Point and Distortion Point of Aminolysis Products.

Product	Peak 1			Peak 2			Distortion Point Peak (°C)
	Melting Point (°C)	Melting Point Peak (°C)	Heat of Melting Point Peak (J/g)	Melting Point (°C)	Melting Point Peak (°C)	Heat of Melting Point Peak (J/g)	
AM	187.66	199.81	72.142	217.13	231.83	92.97	323.25
DM	139.24	157.04	108.85	182.89	213.08	220.17	296.41
TM	150.03	152.89	151.07	179.30	225.64	280.58	324.01

Discussion

In this study, we optimized the procedure conditions by the use of alkanolamines and the products structural investigation was performed.

Alkanolamines such as monoethanolamine, diethanolamine, and triethanolamine were used for the aminolytic depolymerization of PET. The reaction mechanisms have been shown in Figures 1-3. Depolymerization of PET with monoethanolamine has two nucleophilic centers. Nitrogen is more electronegative than oxygen [2]. When PET reacts with diethanolamine and triethanolamine, because of space avoidance around the amine group, hydroxyl groups attacks PET chain, therefore, in PET aminolysis reaction with alkanolamines, the oligoesters obtained contains hydroxyl as terminal groups.

As shown in Table 1, the increased reaction time and ratio of alkanolamines to PET caused a progress to produce monomer, and dimmer and increased reaction mass yield.

The average molecular weight of PET aminolized products was determined based on standard method [17].

In order to assign the average molecular weight ($\overline{Mn}$) of products, the hydroxyl value (HV) and the sum of hydroxyl and amine groups (n) should be determined by using function-based standard procedure (1), and $\overline{Mn}$ of products were calculated by the equation (1).

$$\overline{\mathrm{Mn}} = \frac{\mathrm{n} \times 56.1 \times 1000}{\mathrm{HV}} \qquad (1)$$

According to this standard procedure, the -NH- groups causes interference with -OH groups. The reaction time was increased in order to ascend the participants of both –OH and NH- groups which are essential for determination of average molecular weight.

The effect of three parameters such as time, the molar ratio of alkanolamines to PET and the type of alkanolamines in aminolysis reaction were investigated. As illustrated in Table 2, increase of time and the molar ratio of alkanolamines to PET enhance the reaction progress and consequence smaller oligomers.

The total product nitrogen obtained from aminolysis reactions were measured by standard procedures, and a number of product samples (AM-1, AM-3, AD-1, AD-3, AT-1, and AT-2) which had a lower average molecular weight were investigated by Kjeldahl method and elemental analysis in order to confirm the accuracy of data obtained based on standard procedures. According to Table 3, the results of systematic methods confirm achieved results of practical way. Also whole nitrogen values comparison of systematical and analytical ways with whole nitrogen values obtained from theoretical way shows that the oligoesters chain length in performed reactions (Figures 1, 2, and 3) are almost equal to n=1 and n=0.

According to attained ^{1}H NMR and FTIR spectrums from PET aminolysis products, in obtained products from PET aminolysis reaction with monoethanolamine, the presence of amid bending, tensional peaks in FTIR spectrum, and existent –NHCO- group proton peak in ^{1}H NMR spectrum confirm the showed mechanism in Figure 1. Presence of tensional peaks of the secondary amine group on FTIR spectrum, and existent secondary amine proton peak in ^{1}H NMR spectrum in products from PET aminolysis reaction by diethanolamine, and absence of peaks in the tensional zone of amine groups (caused by tertiary amine forming) in FTIR and ^{1}H NMR spectrums in products (AT1-AT4) from PET aminolysis reaction with triethanolamine, all confirm the showed mechanisms in Figures 2, and 3.

Conclusion

Recycling PET bottle wastes to produce new materials with different properties, is one of the possible ways to remove these wastes from the environment. Concerning to widespread use of this polymer in household and industry, the application of polymeric recycling reactions resulted to functional production, less environmental pollutions, and is economically beneficial. In this study, oligoesters with different average molecular weight were obtained by making changes in various parameters such as time, molar ratio, and type of alkanolamines in several reactions.

In depolymerized products of PET with monoethanolamine and diethanolamine, 2 hydroxyl groups and PET reaction with triethanolamine, four hydroxyl groups were observed at the end of polymer chains. The compound of polyol obtained from aminolysis reactions could be an alternative of polyols used in common synthesizes of polymeric materials in order to produce new industrial polyesters and polymers with noble features, the consequence of this alternation could be a subject of further studies.

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