

RESEARCH OF THE OBTAINING OF BIS(2-HYDROXYETHYLENE) TEREPHTHALAMIDE IN THE AMINOLYSIS PROCESS

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Abstract. *In this work, the process of aminolysis of secondary polyethylene terephthalate (SPET) with monoethanolamine (MEA) at low ratio was investigated. The composition, structure and yield of the products formed as a result of the aminolysis process were studied. aminolysis product was selected in a ratio of 1:4, mixed in hot water at a temperature of 90 ± 2 °C for half an hour, washed and filtered while hot. The solid product remaining on the filter was obtained in second fractions. The filtrate was cooled to room temperature and a white precipitate formed. After that, the precipitated fraction was filtered again. The rest of the filter was dried at a pressure of 0.92 kg force/cm² and a temperature of 75 °C until the mass did not change. The separated second fraction has a melting temperature of 217 °C and a molecular mass of 1000. In the IR-spectrum of the obtained product, the 1,4-substituted aromatic group has a secondary amide group, a methylene group and a primary hydroxyl group.*

We also engaged NMR to get more information. In the NMR ¹H structure of this product, the proton in the amide group (8.59 m.u), the protons belonging to the aromatic group (7.6 m.u), the protons belonging to the hydroxyl group (4.66 m.u), the protons belonging to the methylene group connected to the oxygen atom (3.59 m.u), with the nitrogen atom there are specific signals of protons (3.36 m.u) in the bound methylene group. The ratio of the number of protons (nitrogen, aromatic group, hydroxyl group, methylene, methylene group) is 2:2:1:2:2. According to the NMR ¹³C spectrum analysis of the final product, there is no branching in its molecule.

Thus, based on DTA, NMR, IR analysis, it can be noted that the product of aminolysis is BHETA. Up to 73% yield of bis(2-hydroxyethylene) terephthalamide was achieved by aminolyzing SPET with MEA in a catalyst-free environment.

Keywords: *monoethanolamine, terephthalamide, aminoethylethanolamine, aminolysis products.*

Introduction. A million plastic bottles are purchased every minute around the world and up to five trillion of plastic bags are used per year. In total, half of the plastic produced is used once. This creates global environmental problems. Polyethylenterephthalate makes up the bulk of them. Approximately 56 million tons of PET are produced worldwide each year, most of which are used for disposable consumer items and disposable packaging materials [1]. The methods of chemical processing of SPET are divided into several groups, which are: methanolysis, glycolysis, hydrolysis, ammonolysis, aminolysis and other methods [2]. PET degradation product with aminospirts, specifically BIS - (2-hydroxyethyl) terephthalamide.[3] which had primary and secondary aminogroups along with hydroxyl groups for the Aminolysis reaction. Not much studied aminoethylethanolamine (AEEA) has been reported today. This shows the possibility of obtaining a coating product from polyetherpolyol based on the pet waste product [4]. In the work of Ramin Shamsi and Majid Abdouss, the formation of BIS (2-hydroxyethylene) terephthalamide (BHETA)

by aminolysis and the possibility of using this product as a raw material in polyurethane extraction have been studied [5] the use of triethanolamine for Aminolysis has led to the formation of some recent liquid products. The possibility of applying them to epoxy tar-based compositions as by-products has been studied and their properties have been determined. Studied chemical degradation of secondary pet with diethylentriamine, polyamines such as triethylentetramine, and their mixtures, as well as mixtures of triethylentetramine and p-phenylenediamine or triethanolamine, and properties of products [6].

Since polyethylenterephthalate is a thermoplastic polymer, it makes it possible to obtain the raw materials necessary for various soxas using a destructive reaction from it. Aarti More and Shashank Mhaske, for example, used secondary polyethylenterephthalate waste as an anti-corrosion modifier based on epoxide developed with depolymerized specialty [7]. This article investigated the dependence of the product Bis(2-hydroxyethylene) terephthalamide (BHETA) and its composition on the conditions under which this reaction is carried out, which is characteristic as a result of the aminolysis reaction of SPET with MEA. Based on the experiments carried out, as a result of a 1:10 change in the molar proportions of the initial substances, the Bis(2-hydroxyethylene) terephthalamide becomes a dressing, leads to a different nebula of the composition of the product, and the result obtained was shown to be used in different Sox [8]. At the same time, in recent years, studies conducted by the above foreign scientists have shown that the processes of amonolysis have great scientific and practical acumen [9-11]. In these scientific works, the process of aminolysis of secondary polyethylenterephthalate with high proportions of monoethanolamine (1:6, 1:8 and 1:10) has been studied and the possibilities of obtaining products based on reaction products such as unsaturated polyethers, polyurethanes and epoxy resins have been shown. R.L Vesnin and A.A. Taking Alalikin SPET with monoethanoamine and triethanolamine at a temperature of 160 oC without a catalyst, in a ratio of 1:6 mol/mol, for 3-4 hours, resulted in an output yield of 73% BHETA [9]. In another work, aminolysis has been achieved to obtain a complex polyefirpoliol suitable for polyurethanes by interacting with the amino acid BHETA with 1,4-Butanediol, and its properties have been compared with that of an analogue [10]. Another study observed a 75% increase in product output flour from 69.56% when carried out 1-4 hours with sodium acetate as a catalyst for 1:4 and 1:7 ratios at the same temperature [11]. The following year, Tawfik and others [12] developed an environmentally friendly degradation pathway for aminolization of PET fragments with EA using sunflower as a renewable energy source. The catalysts used were dibutylcalay oxide, sodium acetate and cetyltrimethylammonymbromide. Full PET degradation was achieved within 60 days of exposure to sunlight [13]. The purpose of this work is to study the process of aminolysis of secondary polyethylenterephthalate with monoethanolamine in a low ratio of monomers without the use of catalysts. In most scientific data, it turned out that the level of study of the amine preservative in low proportions is low. The full study of the process of aminolysis of SPET with monoethanolamine, with the aim of identifying the factors that affect it, made our studies 1:4 mol el.we focused on carrying zveno / mol ratio.

Object and methods of research.

When conducting research, the following substances were used: secondary polyethylentereftalate – polyethylentereftalate containers in consumption are ground in a mill, monoethanolamine (GOST 2768-84, produced in the Russian Federation) is the amount of the main substance – 99.3%, density 1,012 g/cm³.

The aminolysis process was carried out in a laboratory device equipped with a three-mouthed, reversible refrigerant, thermometer and Mixer, and monoethanolamine (MEA) was released, slowly raising the reactionary mass to a temperature of 100 °C. The reactionary mass temperature was then gradually raised to 170 °C and 190 °C for 60 Minutes. The process was carried out for 8 hours after the temperature rose to 190 oC. By lowering the temperature of the resulting product to 100 oC, the aminolysis was stirred at 90 °C for 30 minutes by placing a 1:4 ratio of water on top of the product and elephants in a hot state. The filtered liquid was cooled to -2 °C, precipitated, and the precipitated white crystals were filtered again. The filtered products are dried in a vacuum oven at a temperature of 75 °C until a constant mass remains.

Discussion of the results obtained

In order to study the composition, structure and output of the products formed by the aminolysis process, the properties of the synthesized aminolysis products were studied (Table 1).

| SPET : MEA mole ratio | Amount of Amino groups mgKOH / gr | Amount of Hydroxyl groups mgKOH / gr | Dilution temperature, °C | Average molecular mass | Yield of BHETA %, |
|-----------------------|-----------------------------------|--------------------------------------|--------------------------|------------------------|-------------------|
| 1:4 | 503,94 | 491,27 | 217°C | 1000 | 73 % |

Table 1. Physical chemical properties of aminolysis products.

In order to delve deeper into the composition and structure of the aminolysis product, the aminolysis product was initially filtrated in a hot state by selecting a ratio of 1:4 and rinsing in hot water at a temperature of 90±2 oC for half an hour.

The solid product remaining in the filter was obtained in 2 fractions. The filtrate was cooled to room temperature and a white precipitate formed. After that, the precipitated fraction was filtered again.

The residue in the filter was dried at a pressure of 0.92 kg force/cm² and a temperature of 75 °C until the mass did not change. The separated 2nd fraction has a melting temperature of 217 °C and a molecular mass of 1000.

The resulting BHTEA is soluble in dimethylsulfoxide and in water at room temperature (80-90 °C). The melting point of its crystals is 226 °C. The resulting BHETA product was taxied using IR spectra in the “IRAffinity-1” IR spectrum and the KL-js-1000 Thermal Analyzer DSC apparatus.

The resulting product IR-Spector contains the transfer peaks of the following groups. Specific to the hydrogen bond-bonded double amide group at 3356,1556,1209,1159 cm⁻¹, specific to the hydrogen bond-bonded hydroxyl group at 3279,1209,1091,1051,1016 cm⁻¹, specific to the hydrogen bond-bonded hydroxyl group at 2927,2875,2850,1462,1381,1367,727 cm⁻¹, corresponding to methylene typical of the corbonyl guruches in the 1 da amid guruches, 1319,1124 cm⁻¹ is typical of the DA – C-N-guruches, 1500,1462,889 is typical of the 1.4-bedded aromatic people [14].

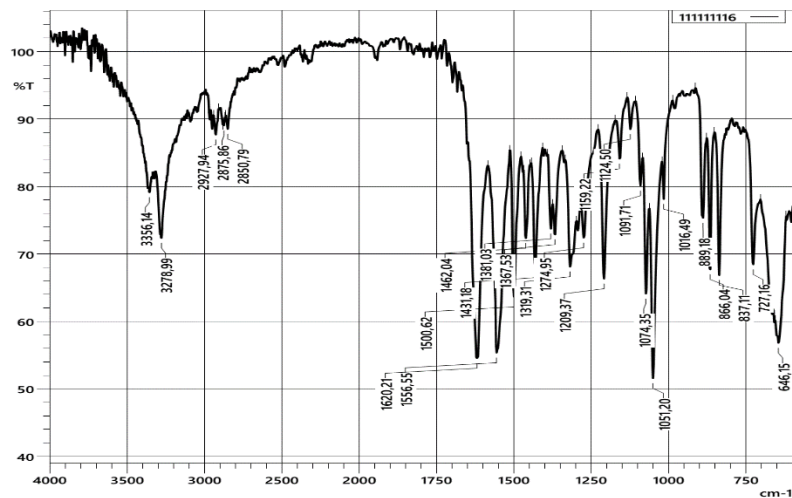


Figure 2. The IR spectrum of the synthesized aminolysis product (SPET: MEA=1:4).

Thus, the aminolysis product contains the 1.4-position-specific aromatic ring double amide group, methylene group and primary hydroxyl groups.

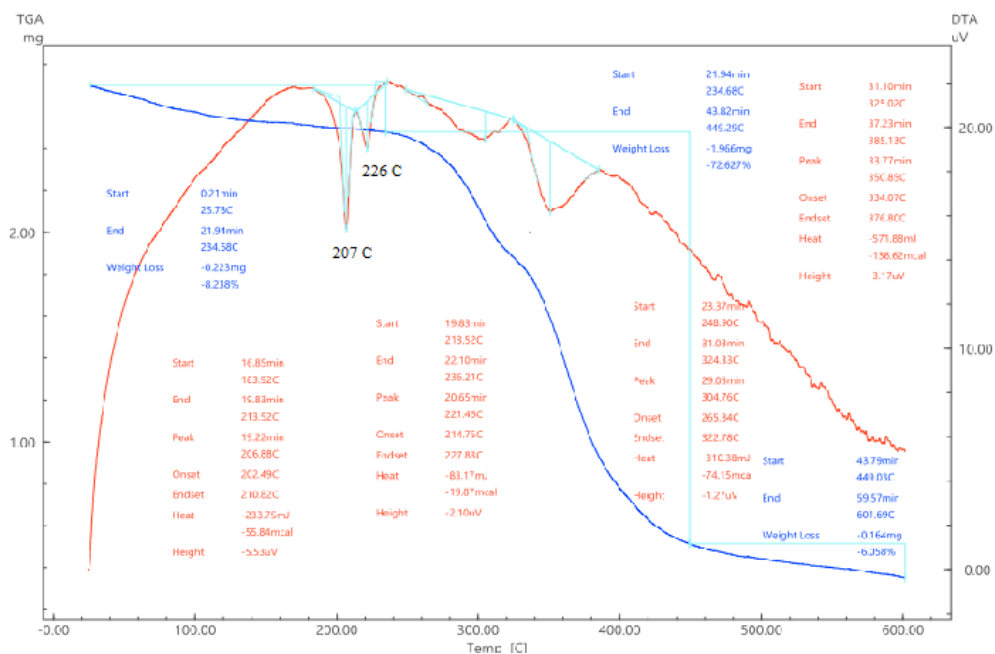


Figure 3. The results of the DTA and TGA approximation of the synthesis aminolysis product (SPET: MEA=1:4 mol el.zveno / mol ratio).

In order to determine the thermophysical properties of the aminolysis product, thermogravimetric analysis TGA, differential thermal analysis DTA analyzes were conducted. The results of the analysis showed that there were several endothermic peaks in the compound formed in the ratio of SPET and MEA = 1:4 mol el.zveno/mol.

The maximum of the enhanced endoeffect peaks occurred at 170 °C, the second at 220 °C, the third at 240 °C, the fourth at 340 °C, and the fifth at 400 °C. The most mass loss occurred between the last three peaks, indicating that it is related to the structure.

We used NMR to obtain complete information about the structure of the aminolysis product. The following signals were observed in the NMR ¹H structure of this product Fig. 4. The proton in the amide group is 8.59, the protons in the aromatic group are 7.6, the protons in the hydroxyl group are 4.66, the protons in the methylene group connected to the oxygen atom are

3.59, and the protons in the methylene group connected to the nitrogen atom are 3.36. The ratio of the number of protons (nitrogen, aromatic group, hydroxyl group, methylene, methylene group) 2:2:1:2:2

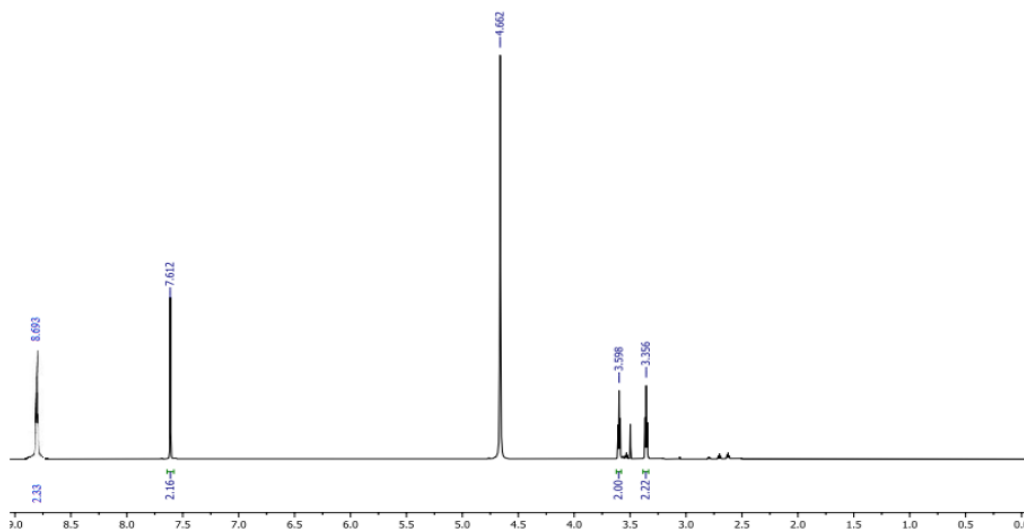


Figure 4. The synthesis involves the ^1H NMR spectrum of the aminolysis product (SPET: MEA=1:4 /hydrazine hydrate).

In the NMR ^{13}C structure of the final product, Figure 5 contains signals of carbons bonded to amide groups at 170, carbon atoms bonded to hydroxyl groups at 62.5, and carbon atoms bonded to amide groups at 42.1 [15]. There is no branching in the molecule, that is, there are no signals characteristic of tertiary carbon atoms.

The obtained results are analogous to the conclusions made in [14,15]. In these works, the amination of IPET under the influence of sunlight was studied in the presence of ethanolamine in the ratio of 1: (3+12) mol: mol [14] in the presence of three different catalysts (sodium acetate, ammonium bromide, dibutyl tin oxide). In both studies, it was noted that bis 2-hydroxy (ethylene terephthalamide) BGTF A was formed as the final product. The structure of BGTF A was studied using spectrophotometric methods. The results of these studies confirm our results.

Thus, based on DTA, NMR, IK analysis, it can be noted that the product of aminolysis is BGTF A. This conclusion confirms the conclusions of authors 5, 8, 14, 15. Different from them, we obtained SPET: MEA without catalyst in 1:4, mol ratio.

Conclusion

Thus, the process of aminolysis of secondary polyethylenterephthalate with monoethanolamine was studied in low proportions without catalysts. It was found that the release of the aminolysis product depends on the level, ratio and reaction time. The structure of the isolated BHETA was studied using IQ, thermic taxa, and was confirmed to correspond to BHETA. The effect of the amount of monoethanolamine on the physicochemical properties of the aminolysis product of secondary polyethylenterephthalate has been studied at the same time it was found that when the amount of monoethanolamine obtained increases by 4 moles, an excess additional cubic amount is formed as a result of the reaction. The formation was clarified in the composition of the products. In muxite without a catalyst with SPET MEA, monoethanoamine was found to be a

bis(2-hydroxyethylene) terephthalamide dressing with an output flour of up to 73% when increased to a ratio of 4 mol.

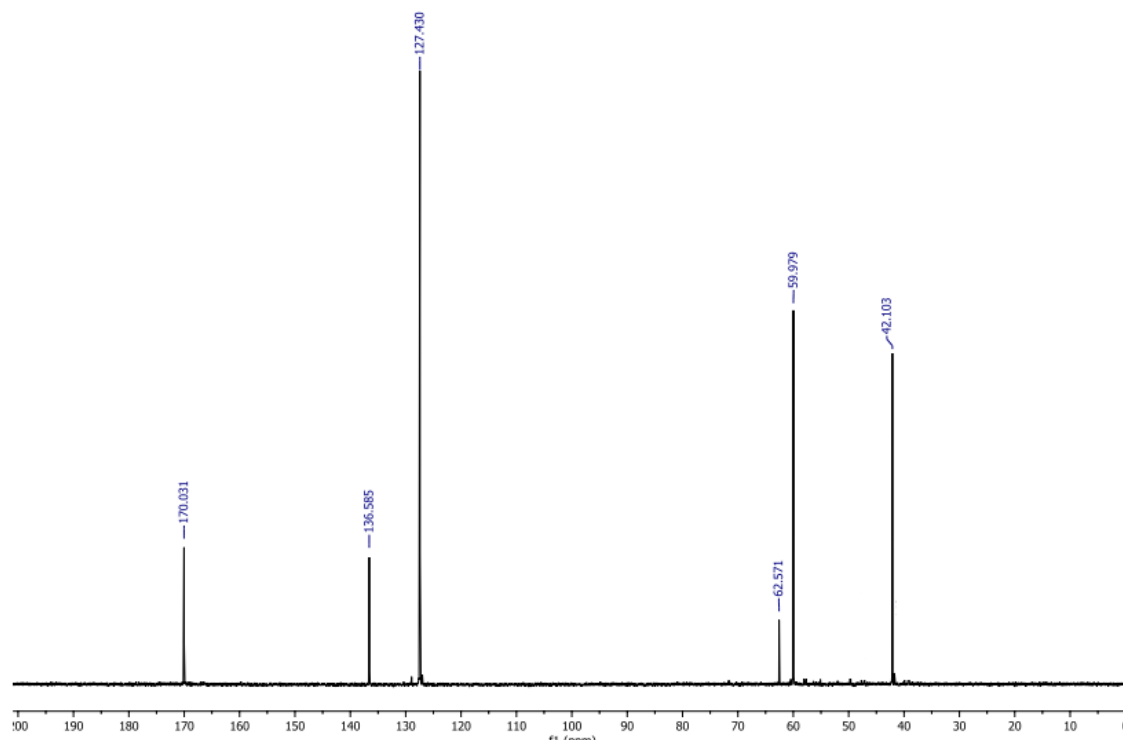


Figure 5. The synthesis involves the ^{13}C NMR spectrum of the aminolysis product (SPET: MEA=1:4 mol el.in zveno / mol ratio).

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