

Obtaining oligoesters by directed glycolytic destruction of polyethylene terephthalate waste

K.A. Kirshanov*, A.Yu. Gervald, R.V. Toms

FGBOU VO MIREA – Russian Technological University

119571, Russia, Moscow, prosp. Vernadskogo, 86

*E-mail: kirill_kirshanov@mail.ru

In this work, oligoesters with terminal hydroxyl groups were obtained by directed glycolytic degradation of polyethylene terephthalate. The possibility of obtaining bifunctional reactive oligomers with an average molecular weight of 865 g mol^{-1} by directed glycolytic destruction via a dissolution-degradation strategy in dimethyl sulfoxide at a low concentration of ethylene glycol (32.3 mass parts per 100 mass parts of polyethylene terephthalate) was shown. This process allows us to partially solve the urgent problem of recycling post-consumer polyethylene terephthalate.

Keywords: *polyethylene terephthalate, PET, glycolysis, recycling, oligoesters, reactive oligomers*

At present, the urgent task of environmental protection is the processing of polymer waste generated both in the processes of obtaining and processing polymers (technological waste) and when using products made of polymer materials (household waste).

Among the polymer waste, a significant part is polyethylene terephthalate (PET) waste. The share of PET waste in the total amount of plastic waste is about 25% or 300 million tons per year [1]. In Russia, about 500 thousand tons of used products made of polyethylene terephthalate goes to landfill every year [2]. Thus, the problem of PET processing is relevant both in the world and in Russia specifically.

Known methods for recycling PET waste are based on mechanical, thermal and chemical processes [3]. Chemical processes for recycling PET waste are of the greatest interest, since they allow one to destruct PET macromolecules and obtain valuable monomers and oligomers. The most widely used processes are hydrolysis, methanolysis, and glycolysis of PET waste [3].

Today, glycolysis is the most relevant area in the chemical processing of PET waste, which is evidenced by the high publication activity in this area (Fig. 1).

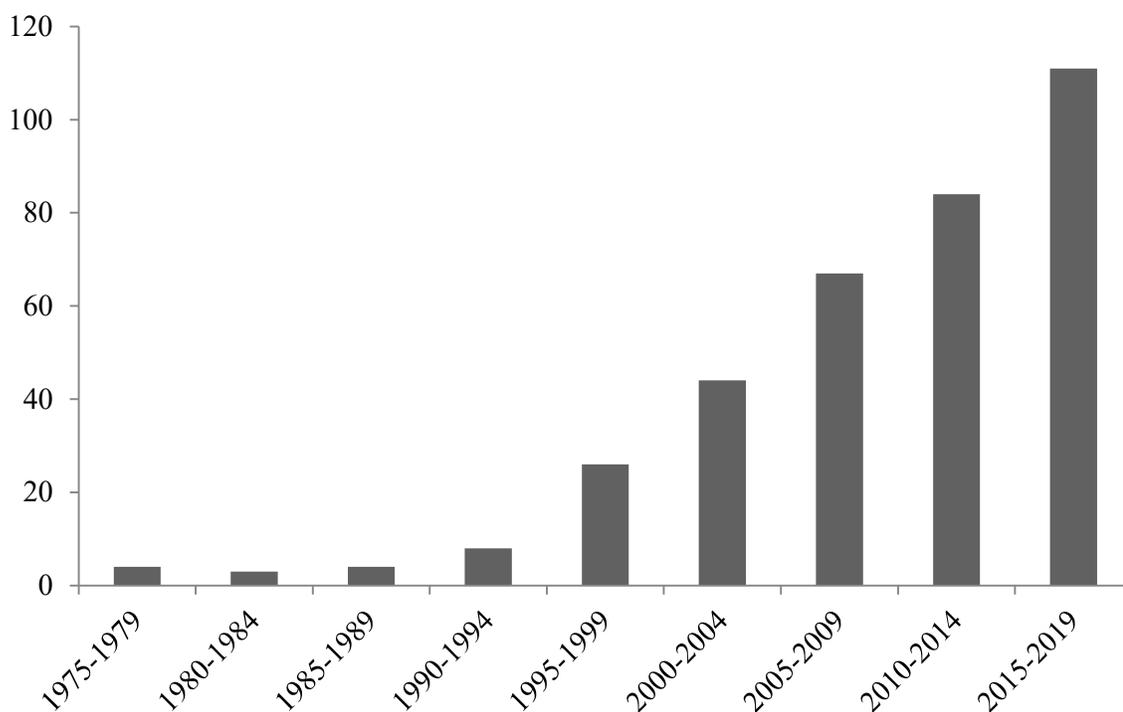
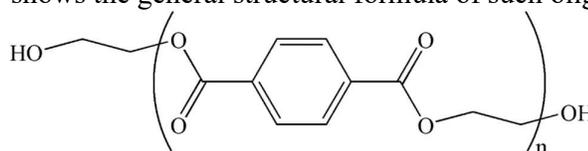


Fig. 1. Number of articles included in Scopus (scopus.com) that mention (in the title, abstract or keywords) PET glycolysis

Directed glycolytic destruction of PET makes it possible to obtain the monomer bis (2-hydroxyethyl) terephthalate (BHET) and reactive oligomers with hydroxyl groups at the ends of the chain [4]. Scheme 1 shows the general structural formula of such oligomers.



Scheme 1. General structural formula of oligomers obtained by PET glycolysis

At the same time, on an industrial scale, PET glycolysis is mainly aimed at obtaining BHET. However, in recent years, interest is also attracted by the preparation of oligoesters, which are widely used.

Various functional copolymers of polyethylene terephthalate, thermoplastic polyester elastomers [5], polyurethane foams [6] and polyurethane elastomers [7, 8] are obtained on the basis of oligoesters. They are distinguished by the degree of crystallinity, modulus of strength, flexibility and thermal properties [9]. Depending on the requirements for these materials, oligomers with molecular weights from 400 to 3500 g mol⁻¹ are used.

Such reactive oligomers can be synthesized from BHET, which is obtained by glycolysis of PET and, as already mentioned, by glycolytic degradation of PET to oligomers. The first method has more technological stages, and the resulting oligomers have molecular weights below 450 g / mol, which is insufficient for their use in the production of polyester and polyurethane materials, as well as as active diluents of epoxy resins [4].

Therefore, the aim of the work was to obtain bifunctional reactive oligomers with terminal hydroxyl groups with the required molecular weight by directed glycolytic destruction of polyethylene terephthalate.

It is known that the kinetics of PET glycolysis and the conversion of ester groups depend on such parameters as the molar ratio of ethylene glycol and PET units, the nature and concentration of the catalyst, the time of the process, and the temperature [10].

Glycolysis of ester groups occurs statistically along the entire chain length of macromolecules; therefore, predominantly oligomers are initially formed in the system. Consequently, for the preferential production of oligomers, it is advisable to carry out the process at lower concentrations of ethylene glycol than for the production of BHET monomer. Therefore, ethylene glycol was used in this work in a molar ratio to PET units of 1:1.

Various catalysts are used for PET glycolysis [11]. The most studied and frequently used catalysts for glycolytic depolymerization are zinc, magnesium, cobalt acetates, lead oxide, metal salts and oxides. The effect of catalyst concentration on the kinetics of glycolysis depends on its chemical nature. In [11], zinc acetate was used with its molar ratio to PET units equal to 1: 245.

Increasing the temperature increases the rate of the glycolysis reaction and conversion. However, its maximum value is limited by the boiling point of ethylene glycol under the reaction conditions. Therefore, glycolysis was carried out at temperatures below 197 °C.

Post-consumer PET plates with a size of 5.0 × 5.0 × 0.6 mm, ethylene glycol (EG), dimethyl sulfoxide (DMSO), and zinc acetate (Sigma Aldrich) were used as materials for glycolysis. EG and DMSO were previously purified by vacuum distillation.

Since glycolysis at a low concentration of ethylene glycol is preparatively difficult, the process was carried out via the dissolution-degradation method [12]. The method is based on introducing a solvent into the system, in which PET swells and dissolves. The introduction of a solvent makes it possible to significantly accelerate the destruction of PET and to carry it out with an equimolar concentration of ethylene glycol relative to the PET units or lower. In this case, the system goes from heterogeneous to homogeneous.

Glycolysis of PET was carried out in a 250 ml flask under reflux. The temperature of the reaction mixture was maintained at about 190 degree. The formulation included 100 mass parts of PET, 400 mass parts dimethyl sulfoxide solvent, 1 mass part zinc acetate catalyst, the concentration of ethylene glycol was varied from 32 to 194 mass parts. After the completion of the process, the hot solution was separated from the remnants of unreacted PET and transferred to 1000 ml of water, the resulting system was cooled at a temperature of 6 °C for two hours. Then the precipitate was filtered off.

The PET conversion was measured gravimetrically by the method [4], the glycolysate was studied by DSC on a DSC 204 F1 Phoenix® calorimeter (NETZSCH Geratebau GmbH, Germany) and FTIR spectroscopy on a Spectrum 65 FT-IR spectrometer (Perkin Elmer, USA). Table 1 shows the conditions for obtaining oligoesters and their characteristics.

Table 1. Conditions for obtaining samples and their characteristics

Sample	Reaction type	The molar ratio of EG to PET units or to DMTP	Temperature, °C	The molar ratio of Zn (OAc) ₂ to PET units or to DMTP	MM, g mol ⁻¹	PET conversion in 120 minutes, %	Position of peaks on the DSC curve, °C
1	Direct synthesis	2,5:1	195	1:100	245	87	107,1
2	Glycolysis	6:1	190	1:100	341	83	107,6 129,0 217,4
3	Glycolysis	1:1	190	1:100	865	57	240,9

Sample No. 1 is BHET obtained by reacting dimethyl terephthalate with ethylene glycol, which was purified by recrystallization in water. Sample No. 2 is a glycolysate obtained with an excess of ethylene glycol (194 mass parts of EG per 100 mass parts of PET), the PET conversion in 20 minutes was 83%. Sample No. 3 is a glycolysate obtained at a low concentration of ethylene glycol (32.3 mass parts of EG per 100 mass parts of PET), the PET conversion in 20 minutes was 57%.

Figure 2 shows the DSC curves for these three samples.

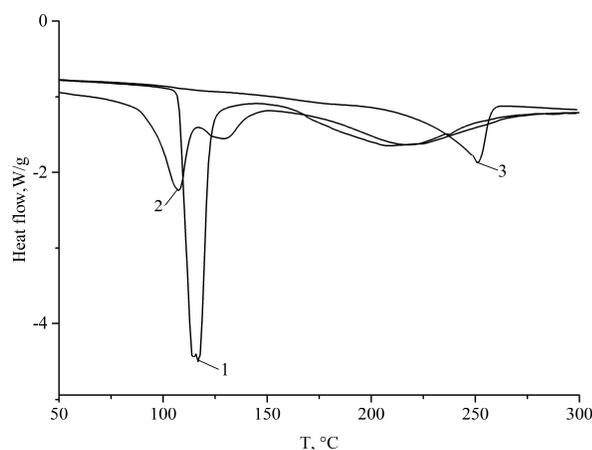


Fig. 2. DSC curves for samples 1 (synthetic BGET), 2 (glycolysate with an excess of EG) and 3 (glycolysate with a low concentration of EG), inert medium - argon, scanning speed - 10 deg min⁻¹

On the DSC curve for sample 1 (Fig. 2), one can observe a peak corresponding to a temperature of 110 °C, which, according to the data, corresponds to the melting of BHET [13]. The second flatter peak corresponds to the melting of residual dimethyl terephthalate and oligomer impurities, as well as to the boiling of residual ethylene glycol. The DSC curve for sample 2 (Fig. 2) also contains a BHET peak, as well as a peak corresponding to the melting point of the dimer, about 130 °C. The third peak is responsible for the melting of the trimer (about 210 °C), higher oligomers, and the boiling of residual ethylene glycol [13]. On curve 3 (Fig. 2) one peak with an onset at about 110 °C can be observed. It can be assumed that it corresponds to the melting of higher oligomers and a small admixture of monomer, dimer, and trimer, as well as to the boiling of residual ethylene glycol.

Figure 4 shows the FTIR spectra of the obtained samples.

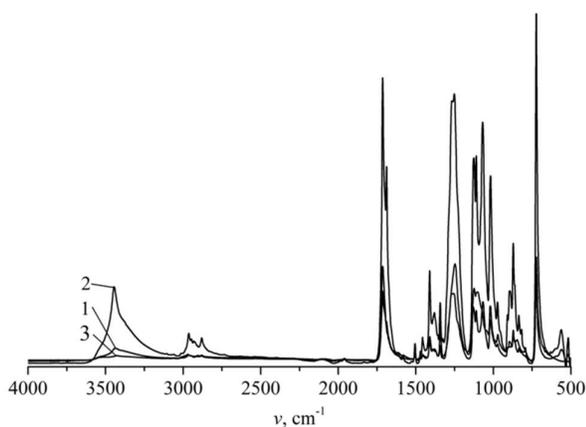


Fig. 3. IR-Fourier spectra of samples 1 (synthetic BGET), 2 (glycolysate with an excess of EG) and 3 (glycolysate with a low concentration of EG)

The FTIR spectrum of BHET (sample 1) corresponds to the data presented in the article [14]. The spectra of samples 2 and 3 differ from each other and from the spectrum of sample 1 only in intensity; the position of the bands approximately coincides. The correlation coefficient of the spectra of samples 2 and 1 was 96 % (correlated), which indicates the predominant formation of BHET, samples 3 and 1 was 85 % (do not correlate).

The number average molecular weight was determined from the ratio of bands corresponding to frequencies of approximately 3350 cm⁻¹ for terminal hydroxyl groups and 1720 cm⁻¹ for carbonyl groups in the chain [14]. The number average molecular weight for sample 2

was found to be about 340 g mol^{-1} , which corresponds to the data [4], for sample 3, it was found to be about 865 g mol^{-1} .

Thus, the absence of a melting peak of BHET and the absence of a correlation between the FTIR spectrum of BHET and the spectrum of sample 3 obtained by glycolytic destruction at a low concentration of EG confirms the assumption that oligomers are predominantly formed at a low concentration of ethylene glycol. It has been shown that due to the successive transfer of the reaction system into one phase upon dissolution of PET, it is possible to successfully carry out glycolytic destruction with low concentrations of ethylene glycol to obtain oligomers. In the case of a heterogeneous reaction without a solvent, the process will proceed to deep conversions on the surface of PET particles, and BHET is predominantly formed, and the bulk of PET does not enter into the reaction. The proposed method was used to obtain reactive bifunctional oligomers with terminal hydroxyl groups and a molecular weight that meets the requirements for the production of various polyester and polyurethane materials or use as active diluents.

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