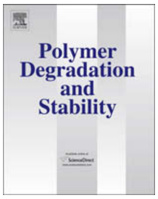
Polymer Degradation and Stability 94 (2009) 240–245

Contents lists available at ScienceDirect

Polymer Degradation and Stability

journal homepage: www.elsevier.com/locate/polydegstab



Theoretical study of the transesterification reaction of polyethylene terephthalate under basic conditions

Yusuke Asakuma*, Kyuya Nakagawa, Kouji Maeda, Keisuke Fukui

Department of Mechanical and Systems Engineering, University of Hyogo, Himeji, Hyogo 671-2280, Japan

ARTICLE INFO

Article history:
Received 4 September 2008
Received in revised form
17 October 2008
Accepted 25 October 2008
Available online 19 November 2008

Keywords:
Polyethylene terephthalate
Activation energy
Electrostatic potential distribution
Depolymerization

ABSTRACT

The depolymerization reaction of polyethylene terephthalate (PET) was analyzed using a computational chemistry approach. The reaction is a type of transesterification reaction using alkoxide. In this study we employed the calculated optimum structure, electrostatic potential distribution, activation energy, electric charges and pathway to investigate the mechanism. We found that the tetrahedral intermediate produced by ring formation with alkoxide is an essential feature of the depolymerization process. Moreover, there is a possibility that a PET molecule is depolymerized by multiple alkoxides at the same time. However, the effects of degree of polymerization and the position of attack by the alkoxides do not strongly influence the reactivity.

1. Introduction

Polyethylene terephthalate (PET) is used extensively in the manufacture of fibers, photographic films a2nd bottles for soft drinks. However, the amount of PET waste is increasing drastically and so a recycling process must be established for the preservation of resources and the protection of the global environment. There are three methods available to reduce the usage of natural resources by recycling plastic waste: physical, thermal and chemical recycling. Chemical recycling (feedstock recycling) chemically decomposes the PET waste into the original feedstock monomers and is of great interest for preventing hygiene and smell problems. When pure monomers are obtained, a PET resin with excellent performance can be resynthesized. In recent years, several processes of PET depolymerization by hydrolysis and alcoholysis have been reported with different depolymerizing agents and operating conditions [1–4]. The most studied chemical recycling reaction is that between PET and a mono alcohol, diol or other solvents under acidic or basic conditions [5–7]. However, a comprehensive understanding of the molecular interactions between PET and alcohol (alkoxide) is necessary for unraveling the details of the depolymerization mechanism.

In this study, a theoretical analysis was conducted to further study the PET depolymerization. Experimentally, PET is depolymerized to ethylene glycol (EG) and disodium terephthalate (Na_2-TPA) in boiling EG with sodium hydroxide under atmospheric pressure. The Gaussian software package was selected from several available computational chemistry programs to simulate the EG alkoxide and the periodic structure of PET because it provides comprehensive molecular information such as optimized structures and electrostatic potentials (ESP) [8,9]. Computational chemistry has been never applied to PET depolymerization and this investigation is the first such quantum chemistry attempt. Various data obtained from these calculations, such as the optimum structure, ESP, electric charge and reaction path were useful for the analysis of the depolymerization mechanism. A comparison of such simulation data with conventional experimental kinetic data will assist in the general understanding of the fundamental behavior of polymer degradation.

2. Computation method

The depolymerization reaction of PET illustrated in Fig. 1 is a kind of transesterification reaction involving the addition of alcohol under basic conditions. The reaction proceeds via the exchange of the alkoxyl group of an ester compound with that of another alcohol. The attachment of the alkoxide breaks the single bond between the carbon and oxygen atom of the carboxyl group as shown by arrows in Fig. 1, and the PET is gradually decomposed into smaller components. Eventually, disodium terephthalate (Na_2-TPA) and EG are produced. Experience suggests that the transesterification reaction should proceed via a tetrahedral intermediate, or transition state, formed when the carbonyl carbon is attacked by alkoxide [10,11]. The characteristics of

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* Corresponding author. Fax: +81 79 267 4847.
E-mail address: asakuma@eng.u-hyogo.ac.jp (Y. Asakuma).

0141-3910/$ – see front matter © 2008 Published by Elsevier Ltd.
doi:10.1016/j.polymdegradstab.2008.10.029

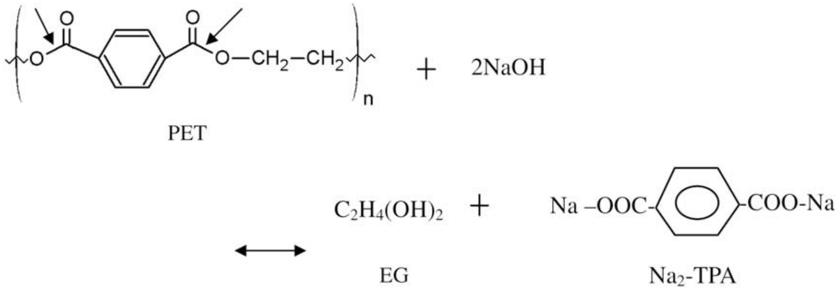

Fig. 1. Depolymerization reaction of PET.

transesterification have been previously considered in terms of activation energy considerations [12,13]. In this study, quantum data concerning the transition state is derived from calculations using the Gaussian software (Gaussian R 03W Ver. 6, Gaussian, Inc.) [12,13]. To simulate the mechanism of the transesterification reaction of PET, a two-stage procedure was adopted as follows.

First stage: calculation of the optimum structure of the ground and transition states. The molecular structures of the ground state (PET and alkoxide of EG) and the transition state during PET transesterification were simulated. The activation energy of the depolymerization reaction was obtained from the optimized structures calculated as the minimum energy configuration from an initial appropriate coordination of the atoms. The basis set used in this calculation is HF/STO-3G* [14,15].

Second stage: calculation of the ESP distribution of PET and alkoxide using the output data from the first stage.

Although a more complex atomic orbital basis set is more accurate for simulating large molecules [16], a simple basis set (HF/STO-3G*) was used because of excessive computation times required by the more complex basis set. The difference of the averaged ESP between the simple and complex basis set is within 6% and the same trends were obtained from both basis sets.

Each electron density has different values of the ESP distribution, therefore, the distribution must be compared at the same isosurface value [17]. In this case, the ESP distribution is visualized for an isosurface value of electron density = 0.001 [electron/au^3].

3. Results and discussion

3.1. Electrostatic properties of PET and alkoxide

The ESP distribution of EG alkoxide is shown in Fig. 2. Here q(O) is the Mulliken charge of the oxygen atom, which has the highest value in the molecule. In the case of EG alkoxide, there are two *cis* and *trans* conformations. When the oxygen atoms are oriented on the same side of the carbon–carbon bond, the compound is referred to as *cis*-EG, whereas, when the oxygen atoms are arranged on opposite sides, it is referred to as *trans*-EG. The ESP distribution and the Mulliken charge both indicate that negative charge concentrates on the oxygen atom due to its high electronegativity. However, in the case of *cis*-EG, the charge is reduced because the two oxygen atoms share one hydrogen atom. The ESP distribution is closely related to the charge, and so the negative charge distribution, shown in red and orange[1], indicates stronger nucleophilicity. In the calculations described below, only results of the depolymerization reaction by *trans*-EG alkoxide are shown because the *trans* conformation is more stable in the solution than is the *cis* conformation.

The results of calculations of the Mulliken charge and ESP distribution of PET are shown in Fig. 3. Here, the Mulliken charge of the carbonyl carbon becomes the most positive value of all the atoms in PET. This occurs because the two oxygen atoms of the carboxyl group induce an electron shift from the carbon atom due to their higher electronegativities. Therefore, the ESP distribution of PET provides a quantitative indication of the electrophilicity of the carbonyl carbon atom. Therefore, the depolymerization reaction occurs via the nucleophilic attack of the EG alkoxide oxygen at the electrophilic carbonyl carbon of PET. Moreover, the formation of a hydrogen bond between the hydrogen atom of the alkoxide and the carbonyl oxygen can become the driving force for a stable transition state of the transesterification reaction. Such a transition state, as shown in Fig. 4, appeared for every calculation and was stable in the optimized structure. It is a tetrahedral intermediate with a pentagonal ring. The energy difference between the ground and transition states equates to the activation energy for the reaction.

3.2. Effect of degree of polymerization on activation energy

Normally, the degree of polymerization of PET is 100–200 and it is impossible to calculate the optimum structure of such a large molecule. To gain insight into the role of the length of the polymer chain, we performed calculations for the depolymerization reaction for PET molecules ranging from a dimer to a decamer (2–10 structural units) and the results are shown in Fig. 5. The values of the activation energy remain very constant regardless of the degree of polymerization as long as the depolymerization is of a PET of more than three structural units (trimer). We expect that this tendency will be quantitatively maintained for PET with more structural units and therefore we can use the activation energy result for a short chain.

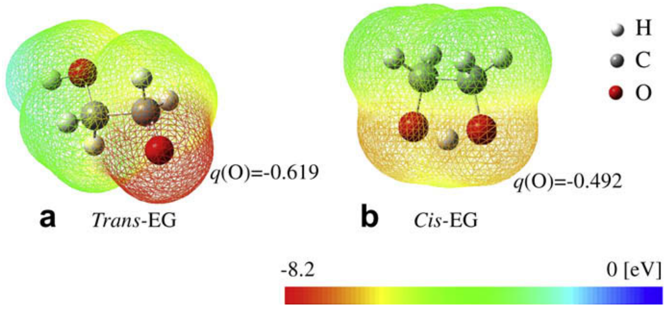

Fig. 2. Electrostatic potential distribution for alkoxide. (a) *Trans*-EG, (b) *cis*-EG.

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[1] For interpretation of the references to color in this text, the reader is referred to the web version of this article.