

# Depolymerization Scheme of Polyethylene Terephthalate in Supercritical Methanol

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Depolymerization scheme of polyethylene terephthalate (PET) in supercritical methanol was investigated to develop a chemical recycling process for post-consumer PET products. PET with a high polymerisation degree was depolymerized in a batch reactor at temperature 553 – 593 K under the estimated pressure 13 – 16 MPa. In addition to PET with a high polymerisation degree, PET with a low polymerisation degree such as oligomer, bis-hydroxyethyl terephthalate (BHET) and methyl-(2-hydroxyethyl) terephthalate (MHET) were decomposed to reveal the depolymerization scheme of PET in supercritical methanol. Reaction products were analysed with size exclusion chromatography (SEC), high performance liquid chromatography (HPLC), and gas chromatography (GC). The main products in each reaction were dimethyl terephthalate (DMT) and ethylene glycol (EG) that were its monomers. The depolymerization of PET with high polymerisation degree into its oligomer was faster than that of oligomer to its monomers (DMT, EG). BHET was depolymerized into DMT and EG through MHET. The results suggested that the depolymerization of PET with low polymerisation degree into its monomers would be a rate-determining step and that the depolymerization of PET would proceed successively through BHET and MHET.

## 1. Introduction

There is an urgent need to develop waste plastic recycling technology for the environmental conservation and the resources conservation. Polyethylene terephthalate, commonly known as PET, is no exception. The production amount of PET has been on rising year by year for producing fibbers, packaging and containers because of its excellent characteristic features. In recent years, various chemical recycling methods for PET recycling have been developed. Methanolysis in supercritical methanol is one of the promising recycling methods.<sup>[1-4]</sup> PET is depolymerized rapidly into its monomers, dimethyl terephthalate (DMT) and ethylene glycol (EG), in supercritical methanol.

To clarify the reaction mechanism of PET depolymerization in supercritical methanol is important applying it to commercial recycle process.

We have reported the continuous kinetics analysis for PET depolymerization in supercritical methanol. [1] The evolution of the molecular-weight distribution (MWD) of depolymerization products and monomers was simulated by the continuous kinetics model. In this work, we investigated the depolymerization scheme in supercritical methanol.

## 2. Experimental

Two types of experimental apparatus (type 1 and type 2) that made by AKICO Co. Japan were used and are shown in Figs 1 and 2. Type 1 apparatus that has a batch reactor (about 5 cm<sup>3</sup> inner volume) was used for analysis of the MWD of depolymerization products and monomers. Type 2 apparatus that has a batch reactor (about 9 cm<sup>3</sup> inner volume) was used for the other experiments. Type 2 apparatus has a special function to swing the reactor to reduce the influence of mass transfer (swing span: 2 cm, frequency of swing: 60 Hz).



Fig.1 Photo of Type 1 test apparatus  
Overview : left side  
Reactor : right side



Fig.2 Photo of Type 2 test apparatus  
Overview : left side  
Reactor : right side

The depolymerization reactions were carried out at temperature 543 - 593 K under the estimated pressure 13 - 15 MPa for the reaction time of 3-60 min. PET of about 2 - 5 g were charged into the reactor and purged with argon. The reactor charged PET was placed in the electric furnace. After reaching a given reaction temperature, the specified volume of methanol was injected into reactor with a plunger pump. The amount of injected methanol was calculated by using Peng-Robinson equation of state to get a desired pressure. In the case of MWD

analysis, PET and methanol were charged into the reactor at the same time. After the keeping the reactor under the reaction conditions, the reactor was cooled quickly and the products were taken out. The products were dissolved in hexa-fluoro-isopropanol (HFIP) or tetrahydrofuran (THF) and analysed depolymerized products by a size exclusion chromatograph (SEC), a high-performance liquid chromatograph (HPLC) and a gas chromatograph (GC). To clarify the depolymerization scheme of PET in supercritical methanol, PET oligomer (trimmer), bis-hydroxyethyl terephthalate (BHET) and methyl-(2-hydroxyethyl) terephthalate (MHET) instead of PET with a high polymerisation degree were depolymerized in the same procedure as PET with a high polymerisation degree.

### 3. Results and discussion

The main products in depolymerization of PET were dimethyl terephthalate (DMT) and ethylene glycol (EG) as shown in Fig.3.

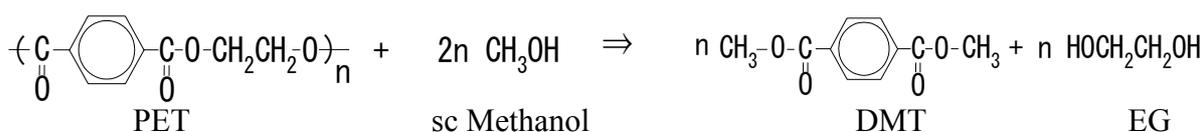


Fig.3 Overview of PET depolymerization in supercritical methanol

Some amount of MHET, BHET, diethylene glycol (DEG) and 2-methoxyethanol (ME) were also produced in present reactions. The yield of monomers is defined as

$$\text{Yield (mol \%)} = \frac{\text{moles of specific products}}{\text{moles of PET units}} \times 100$$

To observe the evolution of MWD of depolymerization products of PET during the reaction, SEC elution curve of depolymerization products at various reaction times were measured. The SEC chromatograms of depolymerization product of PET, PET oligomer and BHET are shown in Fig.4. For all samples, the molecule weight decreased with progress of reaction. After 5 minutes passed, SEC elution curves of each sample became similar shapes. Furthermore, at the reaction time of 10 minutes, the depolymerization proceeded to DMT for all samples. These results suggested that depolymerization of PET with high polymerisation degree into PET with low polymerisation degree such as dimmer, BHET or MHET would proceed in a short time. In

other words, the depolymerization of PET with low polymerisation degree into its monomers would be a rate-determining step. Therefore, the investigation of depolymerization behaviour in this step would be important to reveal the reaction mechanisms of PET depolymerization in supercritical methanol.

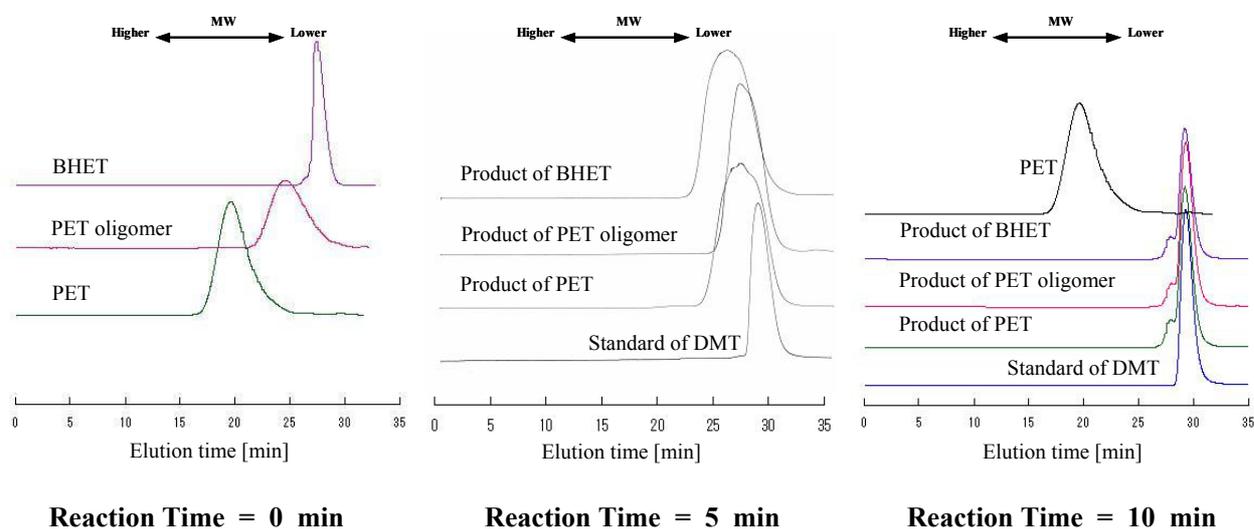


Fig.4 SEC elution curve of decomposition products of various compounds

(Reaction condition : 573 K, 14.7 MPa, sample: methanol=1:5 (weight base) )

Fig. 5 shows the yield of DMT, MHET, and BHET for PET depolymerization as a function of reaction time at 573 K and 14.7 MPa. The yield of DMT increased with reaction time and reached about 80 mol % in 10 minutes. The yield of MHET increased to 36 mol % in 5 minutes and then decreased. The yield of BHET was trace amount and the behaviour of BHET yield was similar to that of MHET yield. The yield of DMT was increasing with decrease of MHET yield. Those results lead to the following reaction pathway in the reaction of PET depolymerization into DMT as reported in our previous paper.<sup>[1]</sup>



To confirm the existence of these reaction pathways, PET oligomer (trimmer), BHET, and MHET were decomposed in supercritical methanol. Fig. 6 shows the yield of DMT, MHET, and BHET as a function of reaction time at 543 K and 14.7 MPa.

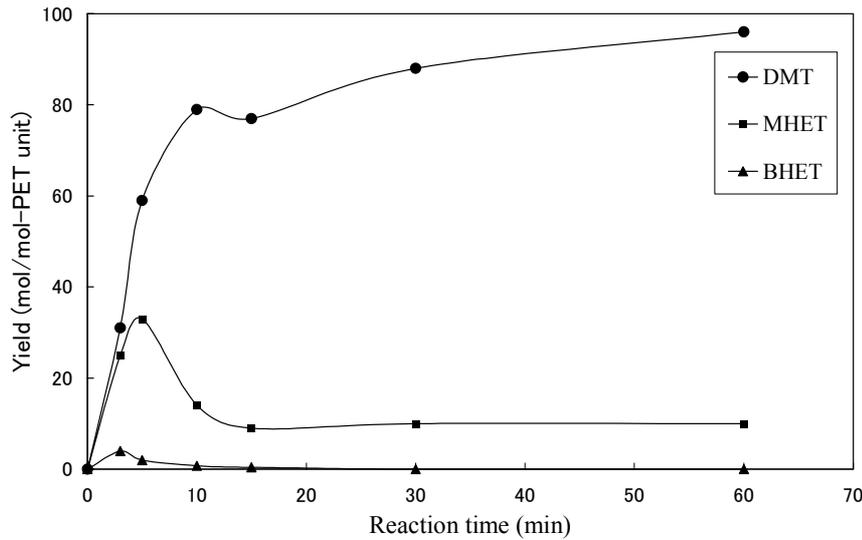


Fig.5 Yields of DMT, MHET and BHET in PET depolymerization in supercritical methanol (Reaction condition : 573 K, 14.7 Mpa, sample: methanol=1:5 (weight base) )

For decomposition of PET oligomer and BHET, the yield of MHET increased initially and then decreased. Meanwhile, the yield of DMT was increasing with decrease of MHET yield. Those behaviours of DMT yield are coincidence with depolymerization of PET with high polymerisation degree. The results suggested that the depolymerization of PET would proceed successively when the reactant molecule became small. Based on our experimental results, the whole scheme of PET depolymerization could be represented by the reaction pathway shown in Fig. 7.

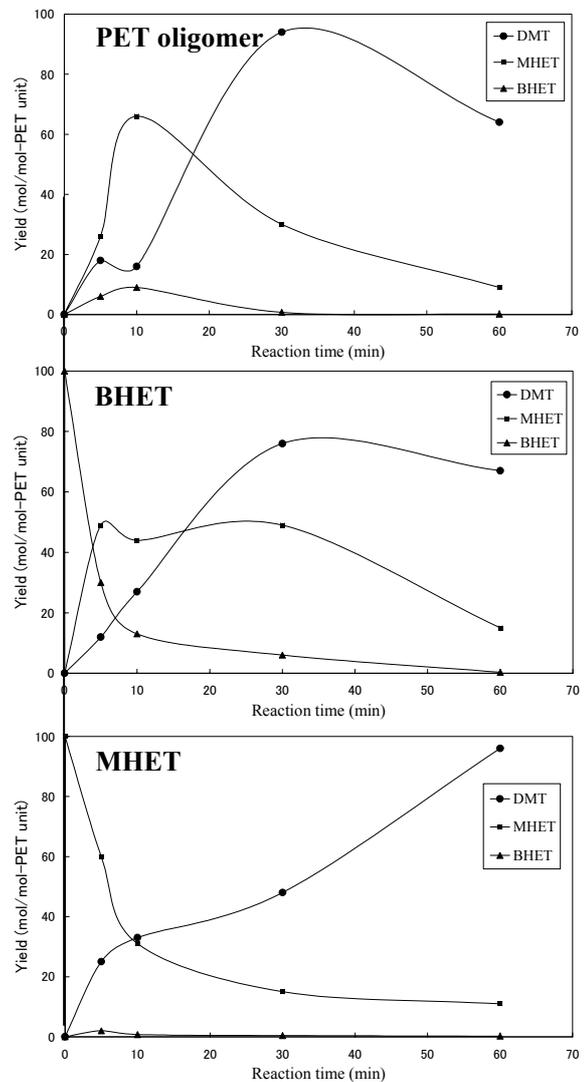


Fig.6 Yields of products in decomposition of PET oligomer, BHET, and MHET (Reaction condition : 543K, 14.7 Mpa, sample: methanol=1:5 (weight base) )

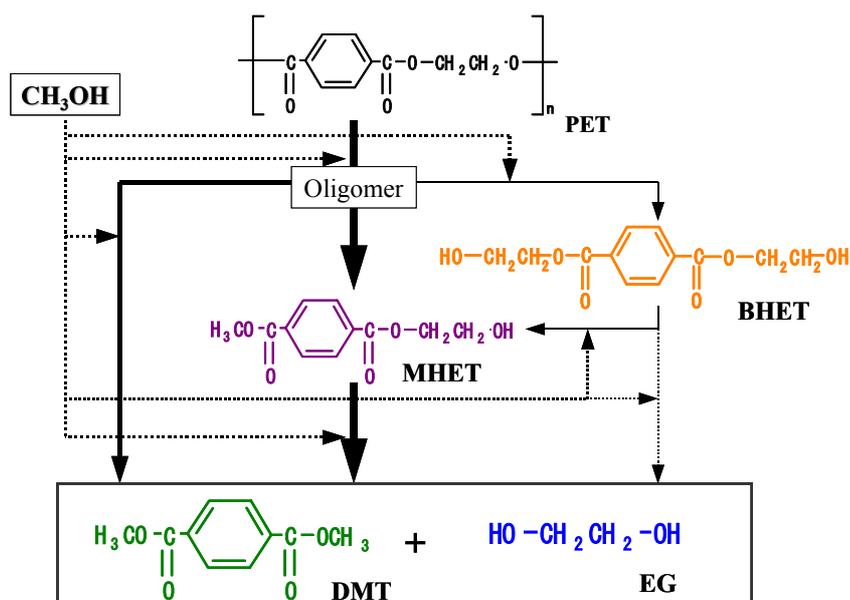


Fig.7 Reaction scheme of depolymerization of PET in supercritical methanol

#### 4. Conclusion

The results suggested that the depolymerization of PET with low polymerisation degree into its monomers would be a rate-determining step and that the depolymerization of PET would proceed successively through BHET and MHET.

#### 5. Acknowledgement

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