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# Depolymerization of polyethylene terephthalate in supercritical methanol

Motonobu Goto<sup>1</sup>, Hiroshi Koyamoto<sup>1</sup>, Akio Kodama<sup>1</sup>, Tsutomu Hirose<sup>1</sup>  
and Shoji Nagaoka<sup>2</sup>

<sup>1</sup> Department of Applied Chemistry and Biochemistry, Kumamoto University,  
Kumamoto 860-8555, Japan

<sup>2</sup> Kumamoto Industrial Research Institute, Kumamoto 862-0901, Japan

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## Abstract

The degradation of polyethylene terephthalate (PET) in supercritical methanol was investigated with the aim of developing a process for chemical recycling of waste plastics. A batch reactor was used at temperatures of 573–623 K under an estimated pressure of 20 MPa for a reaction time of 2–120 min. PET was decomposed to its monomers, dimethyl terephthalate and ethylene glycol, by methanolysis in supercritical methanol. The reaction products were analysed using size-exclusion chromatography, gas chromatography–mass spectrometry, and reversed-phase liquid chromatography. The molecular weight distribution of the products was obtained as a function of reaction time. The yields of monomer components of the decomposition products including by-products were measured. Continuous kinetics analysis was performed on the experimental data.

## 1. Introduction

Plastics are decomposed in supercritical fluids quickly by solvolysis (e.g., hydrolysis, alcoholysis) or pyrolysis. Condensation polymers having ether linkage, ester linkage, or acid amide linkage are easily decomposed into their monomers by solvolysis in supercritical water or supercritical methanol. Hydrolysis in supercritical water [1, 2] and methanolysis in supercritical methanol [3, 4] to achieve polyethylene terephthalate (PET) decomposition have been studied. In this work, we investigated the depolymerization of PET to its monomers in supercritical methanol. The evolutions of the molecular weight distribution (MWD) for the polymer and oligomer were obtained. The concentrations of the monomers and by-products produced in the reaction were measured as a function of reaction time.

## 2. Experimental details

A batch reactor made of a stainless steel tube sealed with Swagelok caps (about 5.4 cm<sup>3</sup> in volume) was used. PET of about 0.3 g and an adequate amount of methanol (0.98–1.41 g)

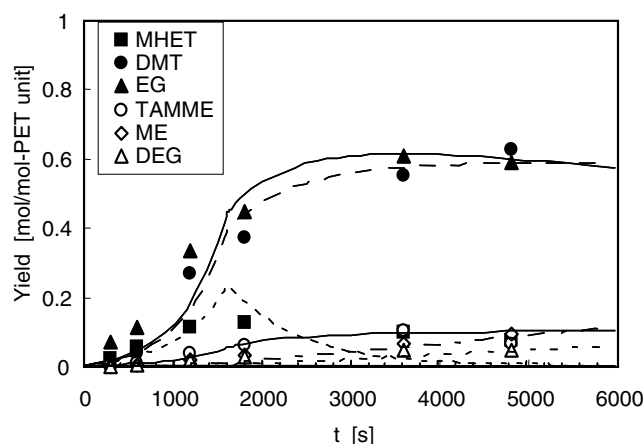


Figure 1. Yields of monomer components for the reaction at 573 K.

for attaining the desired pressure were charged into the reactor and the air in the reactor was replaced with  $N_2$  gas. The amount of methanol charged was calculated by using the Peng–Robinson equation of state to get a desired pressure. The experiments were carried out at a reaction temperature of 573–623 K and the estimated pressure of 20 MPa for the reaction time of 2–120 min. The reaction was started by immersing the reactor in the molten salt bath preheated to the reaction temperature. After a certain time, the reactor was cooled quickly in a water bath to quench the reaction. The reaction products consisted of liquid phase and solid phase, and were analysed by, size-exclusion chromatography (SEC) (Tosoh, TSKgel Super HM-M) using HFIP as a mobile phase with a UV detector gas chromatography–mass spectrometry (GC–MS), and reversed-phase liquid chromatography (RPLC) (Waters, 5C18-MS) using water as a mobile phase with an RI detector.

The PET used was DIANITE PA-500 (Mitsubishi Rayon Co., Ltd, Japan) and its m.p. was 528 K. Dehydrated methanol (Wako Pure Chemical Industries Ltd, Japan) with purity higher than 99.8% was used as a solvent.

### 3. Results and discussion

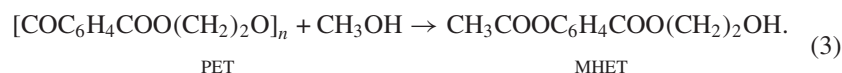
Figure 1 shows the yields of each monomer component as a function of reaction time at 573 K. The yield is defined as

$$\text{Yield (mol\%)} = \frac{\text{moles of specific products}}{\text{moles of PET units}} \times 100. \quad (1)$$

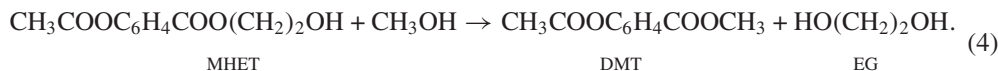
The desired monomer products are DMT and EG, produced by the following methanolysis:



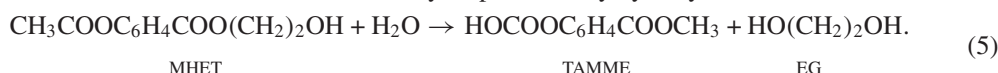
The yield of DMT increased with reaction time and reached 80 mol% at 7200 s. The yield of EG increased to 60 mol% at 3600 s and then decreased gradually for longer reaction time due to the secondary reaction. Methyl-2-hydroxyethyl terephthalate (MHET), which is a 1:1 monomer of DMT and EG, is also produced during the reaction:



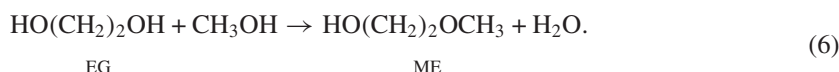
The yield of MHET increased up to 13 mol% at 1800 s and then decreased by decomposition to DMT and EG:



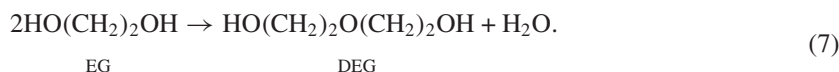
Terephthalic acid monomethyl ester (TAMME) and 2-methoxyethanol (ME) were observed at about 10 mol% in 7200 s. TAMME may be produced by hydrolysis of MHET:



ME is the product of esterification of EG with methanol:



The existence of TAMME indicates that water exists in the reactor, because water is required in the reaction to produce TAMME. Since the initial reactant did not involve water, water must be generated in the reaction. A small amount of diethylene glycol (DEG) dimerized from EG was also observed, up to 2.5 mol%, where the yield of DEG is doubled compared with the yield defined by equation (1) because 1 mol of DEG corresponds to 2 mol of EG:



Water produced in esterification of EG with methanol or in dimerization of EG may contribute to the production of TAMME. Another unidentified by-product related to EG was also observed, in an amount comparable to that of DEG.

The SEC elution curves of the decomposition products at various reaction times were measured. The SEC curves were converted to MWD curves [6].

As the reaction time was longer, the molecular weight of the polymer was decreased. PET with a weight-average molecular weight of about 47 000 (polymerization degree:  $n = 240\text{--}250$ ) was decomposed to oligomer with a weight-average molecular weight of 3000 (polymerization degree:  $n = 15$ ) in 300 s and to oligomer with a weight-average molecular weight of 1000 (polymerization degree:  $n = 5$ ) in 600 s in supercritical methanol. After a reaction time of 1200 s, PET decomposed to components of monomer size, and the DMT peak gradually became larger.

The effect of reaction temperature is shown in figure 2. In the products for reactions at 603 K over 4800 s and at 623 K over 1200 s, white sediment was observed, which may be terephthalic acid produced in the presence of water formed in secondary reactions. The solid sediment became darker for longer reactions at 623 K, which indicates an undesired product in side reactions such as pyrolysis.

For all components, the production rate in the initial part was higher at higher temperature. The yields of DMT and EG at 603 K became lower than those at 573 K at a later time because of secondary reaction. This behaviour is more evident for EG and the yield became constant at 40 mol% after 2000 s. ME and DEG, which are the secondary products from EG, increased with reaction time and their yields are higher at higher temperature. These reactions produce water which works as a reactant in the production of TAMME whose production rate is higher at higher temperature. These results indicate that the decomposition at 573 K was effective for the production of DMT and EG as regards suppressing the production of by-products.

A continuous kinetic model was developed to analyse the reaction behaviour in our previous paper. The calculated yields of monomers are shown in figure 1 as lines. Thus, the continuous kinetics model estimated the decomposition behaviour well for both polymer and monomers.

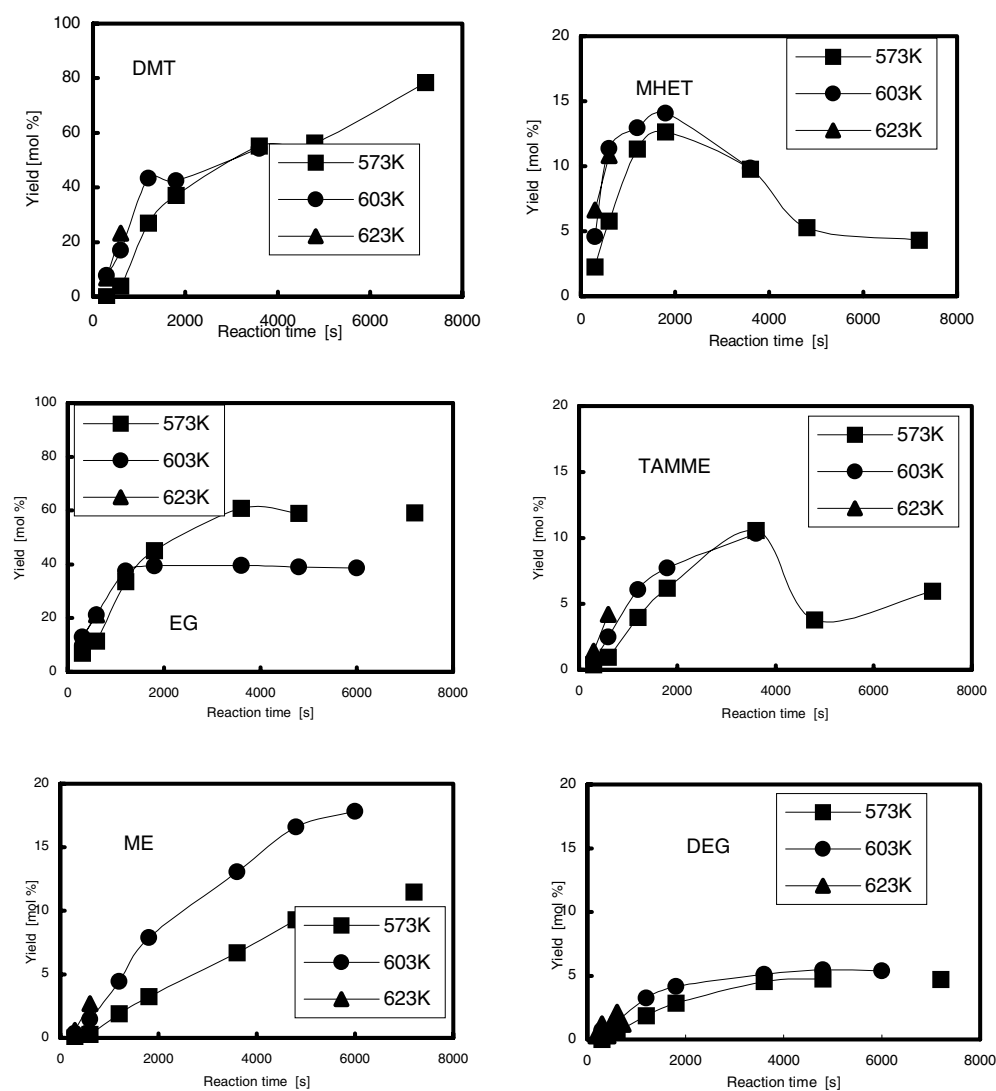


Figure 2. The effect of reaction temperature on the yields of monomer components.

## Acknowledgments

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