

Depolymerization of Polyethyleneterephthalate in Supercritical Methanol

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ABSTRACT: The depolymerization of polyethyleneterephthalate (PET) in supercritical methanol was carried out using a batch-type autoclave reactor. The total conversion and the yield of dimethylterephthalate (DMT) increased with rising temperature. The final yield of DMT at 300°C and 310°C reached 97.0% and 97.7%, respectively. The yield of DMT was markedly increased when the methanol density was 0.08 g/cm³, and leveled off at higher densities. A kinetic model to describe the depolymerization of PET in supercritical methanol was proposed, where the scission of one ester linkage in PET by a methanol molecule produces one carboxymethyl group and one hydroxyl group. The values of the forward reaction rate constant at different temperatures were determined by comparing the observed time dependence of carboxymethyl group concentration with that calculated by the proposed model. The activation energy was evaluated to be 49.9 kJ/mol, a value close to a literature value (55.7 kJ/mol). © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 2102–2108, 2001

Key words: depolymerization; polyethyleneterephthalate; supercritical methanol; methanolysis

INTRODUCTION

Waste plastics are well known for their inability to decompose and degrade in landfill. Moreover, any attempt to incinerate waste plastics tends to produce toxic components and hazardous air pollutants. Recycling of waste plastics has always received much attention as an interesting research topic, although it often requires the most sophisticated technology available today. In recent years, the chemical recycling of waste plastics has been gaining greater interest as a means of obtaining valuable products. Therein, waste plastics are treated chemically to recover low mo-

lecular monomers or other useful compounds. There is a lot of on-going research to find efficient technology to degrade waste plastics; the degradation of waste polymeric materials such as plastics, tires, etc. using supercritical fluid is one promising research area. Supercritical fluids have properties of both liquid and gas phases. The supercritical fluid, which possesses a density close to that of liquid, has the ability to dissolve many components, whereas its high diffusivity and low viscosity also enables it to behave in a manner similar to gas. Such mobile properties of the supercritical fluid tend to maximize the yields of the product in the prescribed reaction time. There are several additional advantages in the usage of the supercritical fluid: rapid rate of decomposition, which enables the apparatus to be more compact compared to the pyrolysis apparatus; reduction in the energy and operation cost due to the relatively low reaction temperature and no need of cata-

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lysts; the byproducts are void of toxic and hazardous components, and further require no secondary treatments before being released into the environment.

Koll and Metzger¹ utilized supercritical acetone to study the degradation of cellulose and chitin, whereas Dhawan et al.² utilized supercritical toluene in their research to degrade polyisoprene and waste rubber. Researchers have studied the degradation of polystyrene (PS) in supercritical acetone in the temperature range of 260 to 300°C.³ The yield of styrene was found to be the highest (35%) among the degraded products when the weight ratio of acetone to PS was fixed at 11.2, equivalent to acetone density, 0.406 g/cm³. The yields of styrene and diphenylbutene (equivalent to dimer of styrene) attained maximum values at a temperature in between 280 and 290°C. The National Institute of Materials and Chemical Research in Agency of Institute of Industrial Science and Technology, Ministry of International Trade and Industry (MITI), Japan, has successfully degraded polyethyleneterephthalate (PET) into terephthalic acid (TPA) and ethyleneglycol (EG) up to 98% using supercritical water under conditions of 400°C and 21.3 MPa. PET, which makes up the majority of plastic beverage containers, possibly decomposes in supercritical fluid media into raw materials such as

dimethylterephthalate (DMT) and EG. Currently, most PET producing facilities employ the process system where DMT is recovered from methanolysis instead of the system where TPA is recovered from hydrolysis, due to the purification process of DMT compared to that of TPA. Moreover, DMT is a more desirable raw material because it exhibits easier mixing with EG and higher activity.

Thus, in this study, the degradation of PET was performed in supercritical states using a batch-type autoclave reactor. Supercritical methanol was found to be the most successful degradation medium for PET. The variation of the distribution of the products with the operating conditions is discussed.

EXPERIMENTAL

The experimental apparatus designed for the degradation of PET in supercritical fluid is shown in Figure 1. The reactor, manufactured by Autoclave Engineers Co., Seoul, was made of stainless steel 316, and had a volume of 1.2 L. Its maximum attainable temperature and pressure were 427°C and 51 MPa, respectively. A water controlled condenser system was installed annex to the reactor to prevent a rapid rise in temperature, which is inevitable during the reaction. The time required

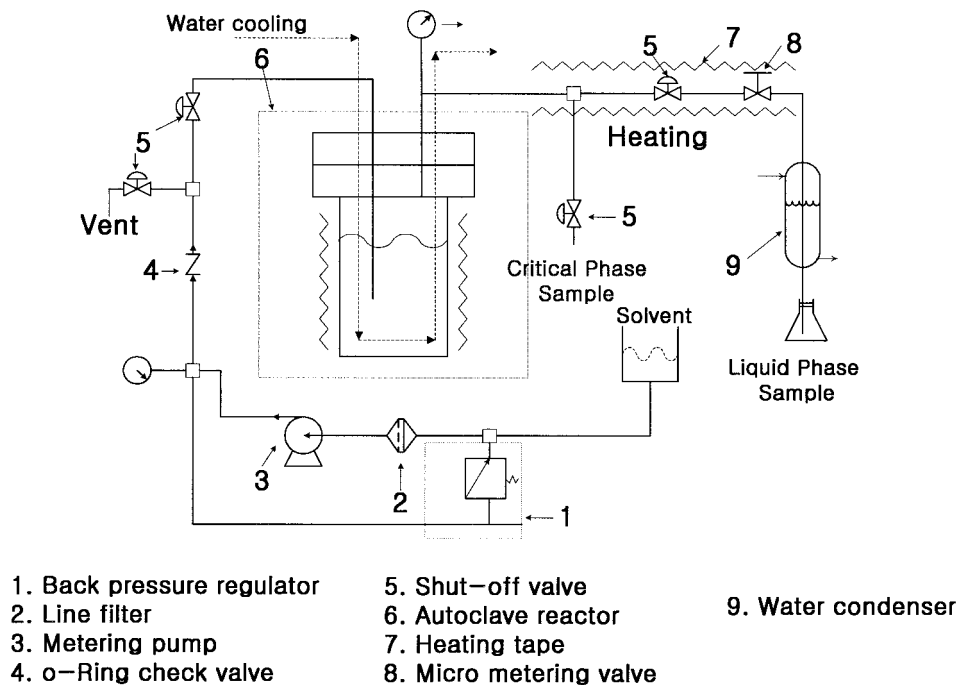


Figure 1 Schematic diagram of experimental apparatus.

to achieve the optimum reaction temperature was limited to within 30 min in order to minimize any undesirable reactions which may have occurred in the heating period. The temperatures of the reactor and furnace were controlled by a PID (Sinko Co., PC600) thermostat, which detects the temperature change within $\pm 1^\circ\text{C}$.

The PET sample to be depolymerized in supercritical methanol was obtained from beverage bottle waste, which was subject to unknown chemical pretreatment. The aluminum lid and the sole of the bottle, which uses high density polyethylene (HDPE) as a major component, were excluded here. High purity HPLC (high performance liquid chromatography) grade methanol was used without any pretreatment.

It was necessary to determine the quantity of methanol charged with the reactor in order to maintain pressure close to the critical one. Peng and Robinson EOS (PR EOS) was used to calculate the density of pure methanol at the critical pressure. Subsequently, the quantity of pure methanol charged with the reactor could be determined from the density calculated by PR EOS. In view of the pressure increase resulting from rising temperature in the reactor, a 100-120 g portion of methanol was fed. The PET samples were cut into pieces to maximize the surface area to promote heat transfer within the reactor. The pieces were 1 cm in length by 1 cm in width with weight that ranged from 10 to 12 g. The pieces were then thoroughly washed with distilled water before being fed into the reactor. Reactions took place at temperatures ranging from 270 to 310°C and at a pressure ranging from 7.0 to 10.1 MPa. The reaction time, up until 70 min, was measured after the reaction temperature reached a prescribed value. To minimize the loss of the products from the reactor, a glass cylinder cooled with water was connected to the products' exhaust valve to prevent the products from spreading into the ambient air.

DMT and impurities, including unreacted PET in the solid state and EG in the liquid state made up the products of the PET depolymerization reaction in supercritical methanol media. The products, mixtures of DMT, EG, and unreacted PET were further separated into solid and gaseous species by filtering them through a glass filter with pore size of 8 μm . DMT crystals, which still could have contained impurities such as oligomer, were collected by freezing the byproduct. The amount of pure DMT had to be thoroughly analyzed after the purification process described be-

low. There are two types of DMT purification processes: the washing process to separate liquid-like impurities such as EG, and the recrystallization process by thermal filtration to separate the liquid-like impurities. In the washing process, the DMT crystals were submerged in distilled water, then mixed by a magnetic bar. The temperature of the solution was maintained at 70°C using a hot plate. Following the washing, DMT solubilized in distilled water was condensed by freezing. During the recrystallization process, nonaqueous impurities and unreacted PET, which were adsorbed onto the DMT products obtained from the above-mentioned washing process with distilled water, were further completely solubilized in methanol at a boiling point (65°C). Methanolic solutions of DMT were filtered through a glass filter with a pore size of 8 μm using an aspirator.

The yield of DMT obtained by the washing and recrystallization process was compared with the theoretical stoichiometric value of DMT, and the percent degrees of production were calculated. The stoichiometric value of 192.17 g/mol was used as a molecular weight of PET's repeating polymer unit. Theoretically, when a 192.17g portion of pure PET is depolymerized, 194.185g (1 mol) of DMT can be produced. In this study, a 10 g portion of PET was used, thus, 10.1049 g of DMT was an expected yield. Theoretically, when 1 mol of DMT is produced, 1 mol of EG is also produced. However, the additives contained in the beverage bottles used here may have lowered the yields. In the present experiment, however, any discrepancies in yields due to the presence of additives were ignored.

Both the purified DMT product obtained through the above-described processes and the standard DMT sample were comparatively analyzed by gas chromatograph (Shimadzu GC-17A, CBP-20 capillary column) and GC-Mass (Shimadzu QP-5000). The product was first dissolved in ethylether, and a 1 μL portion from the solution was analyzed. The liquid product EG was analyzed quantitatively by GC (Shimadzu GC-14A). The amount of injected sample was also 1 μL .

RESULTS AND DISCUSSION

In Figure 2, the dependencies of the unconverted fraction of PET depolymerization and the yield of DMT on the temperature at a reaction time zero and a near-critical pressure of 8.1 MPa for an initial charge ratio of methanol to PET of 10 are

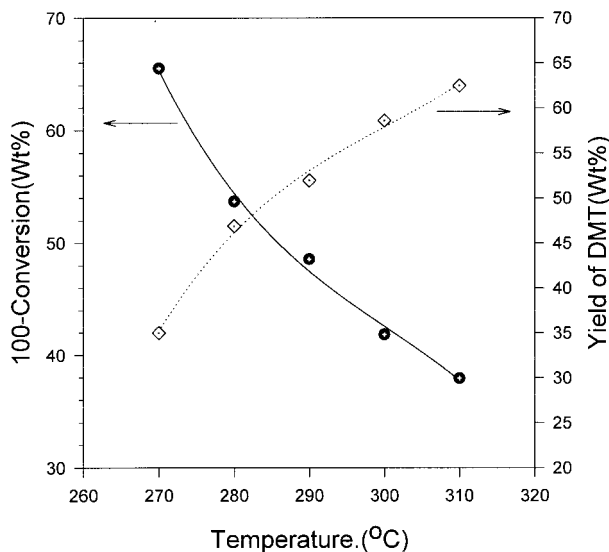


Figure 2 Effect of reaction temperature on unconverted fraction of ester linkage (PET) and yield of DMT at near-critical pressure (8.1 MPa) at an initial charge ratio of methanol to PET of 10.

shown. Both the conversion of depolymerization and the yield of DMT increase with rising temperature. Thus, all experiments were performed above 280°C, where the yields of DMT exceeded 50%.

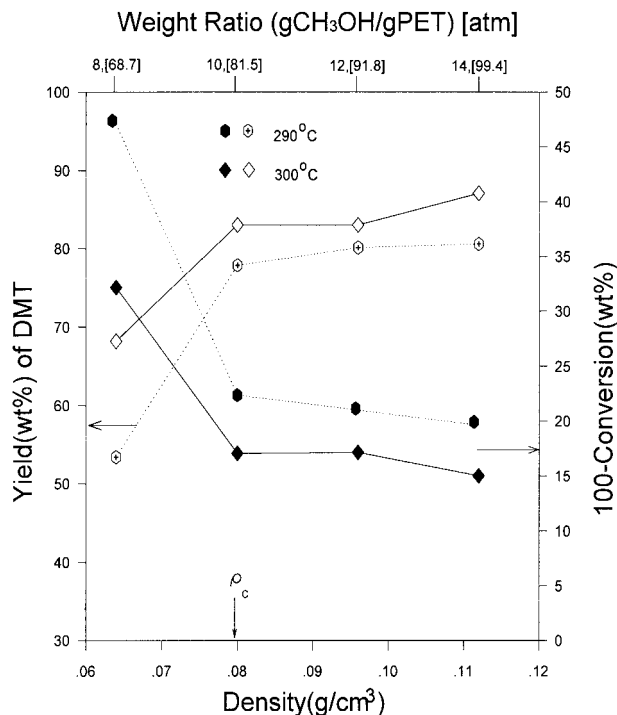


Figure 3 Effect of methanol density on unconverted fraction of ester linkage (PET) and yield of DMT at a reaction time of 10 min.

To determine the reaction conditions regarding fluid density and pressure, the yields of DMT at a reaction time of 10 min were measured as functions of density and pressure. They are shown in Figure 3. The conversion of ester bond in PET and the yields of DMT were sharply increased with an increase in fluid density up to 0.08 g/cm³, which is equivalent to an initial charge ratio of 10 at a pressure of 8.26 MPa. Above these values, both the conversion and the yield increased only slightly. Based on these results, 0.08 g/cm³ of methanol density at 8.26 MPa pressure and 10 charge ratio were chosen as the optimum reaction conditions. Then the yields of DMT were measured at various reaction temperatures and times under these conditions.

The time dependencies of the yields of DMT and EG and the unconverted fraction of PET at temperatures of 280–310°C are shown in Figures 4 and 5. The yield of DMT at 280°C reached 91.3, 93.9, and 94.0% at reaction times of 50, 60, and 70 min, respectively. After 60 min had passed, the depolymerization reaction seemed to be equilibrated. At 300°C, the reaction reached an equilibrium state after 40 min reaction time, and the yield of DMT attained 97%. At 310°C, the reaction also attained equilibrium at 30 min reaction time, and the yield of DMT reached 97.7% which was

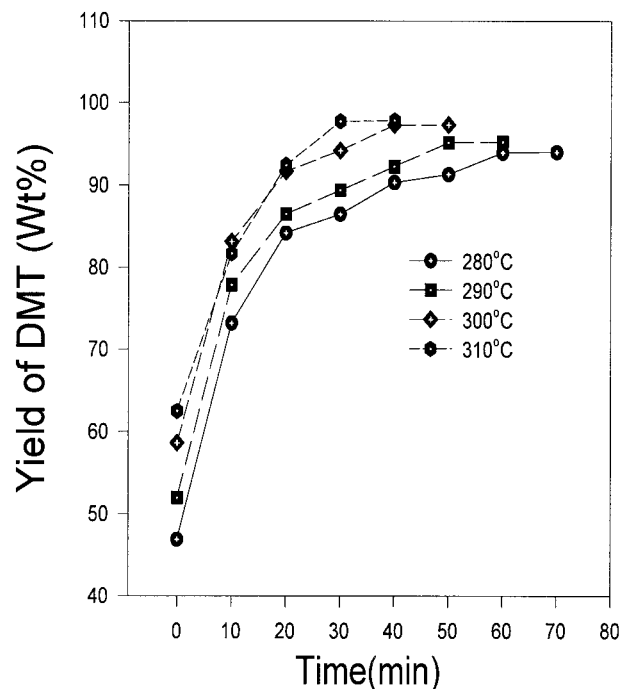


Figure 4 Time dependence of yield of DMT at different reaction temperatures.

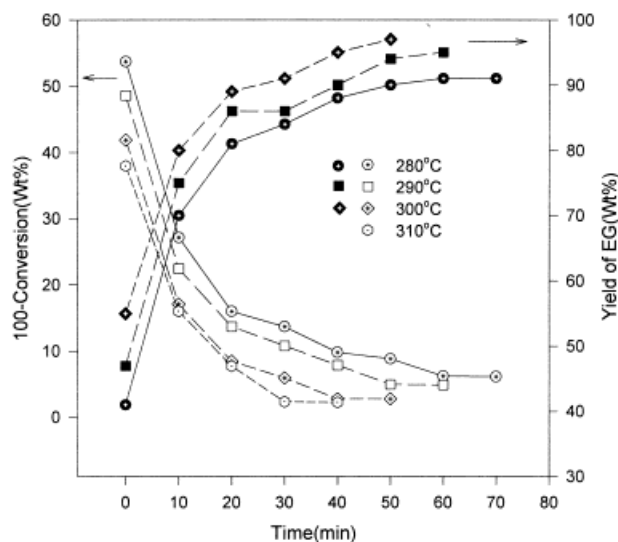


Figure 5 Time dependence of unconverted fraction of ester linkage (PET) and yield of EG at different reaction temperatures.

similar to that at 300°C. The yield of EG at 280°C reached 90, 91, and 91% at reaction times of 50, 60, and 70 min, respectively. The yield of EG was slightly lower than that of DMT. Also, the yields of EG at 300 and 310°C were lower than those of DMT. Theoretically, the formation of 1 mol of EG should result in the formation of the same amount of DMT. It seems that the lower yields of EG compared to those of DMT are presumably due to some inevitable adsorption onto the recovered DMT.

Thus, the depolymerization of PET in supercritical methanol media hereafter was executed under the following conditions: temperature = 300°C, pressure = near-critical pressure (8.26 MPa), reaction time = 40 min or more, initial charge ratio of methanol to PET = 10, and methanol density = 0.08 g/cm³.

Campanelli et al.⁴ proposed a kinetic model to describe the hydrolytic depolymerization of melt

PET. The hydrolysis of PET involves the chemical scission of an ester linkage by a water molecule to create one carboxy end group.

On the basis of a similar concept, a kinetic model to describe the depolymerization process in supercritical methanol media can be constructed. The polymerization of PET in supercritical methanol involves the scission of two ester linkages by two methanol molecules to form two carboxymethyl groups [-C(O)OCH₃] in DMT and two hydroxyl groups (-OH) in EG, as shown in Scheme 1.

The reaction (methanolysis) rate can be expressed as

$$\frac{dC_{\text{COOCH}_3}}{dt} = kC_{\text{EL}}C_{\text{CH}_3\text{OH}} - k'C_{\text{COOCH}_3}C_{\text{OH}} \quad (1)$$

where C_{EL} refers to the concentration of ester linkage, and k and k' denote the rate constant for forward and reverse reactions, respectively.

In view of stoichiometry, $C_{\text{COOCH}_3} = C_{\text{OH}}$, $C_{\text{EL}} = C_{\text{EL},0} - C_{\text{COOCH}_3}$, and $C_{\text{CH}_3\text{OH}} = C_{\text{CH}_3\text{OH},0} - C_{\text{COOCH}_3}$. Then, eq. (1) reduces to

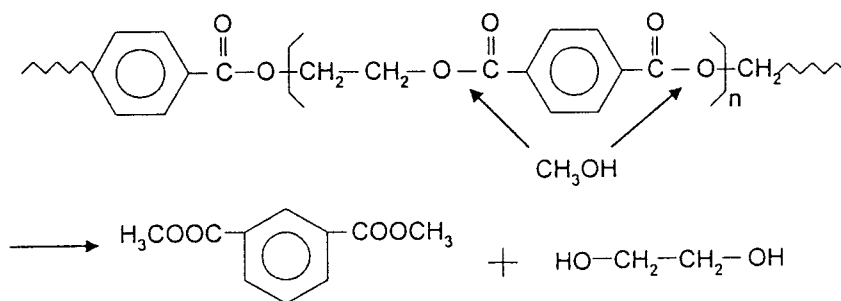
$$\frac{dC_{\text{COOCH}_3}}{dt} = k(C_{\text{EL},0} - C_{\text{COOCH}_3})(C_{\text{CH}_3\text{OH},0} - C_{\text{COOCH}_3}) - k'C_{\text{COOCH}_3}^2 \quad (2)$$

where subscript 0 means the concentration at reaction time zero.

Integration of eq. (2) leads one to the analytical solution for C_{COOCH_3} :

$$\ln \frac{|C_{\text{COOCH}_3} + a - b|}{|C_{\text{COOCH}_3} + a + b|} = -2b(k' - k)t + \ln \frac{|C_{\text{COOCH}_3,0} + a - b|}{|C_{\text{COOCH}_3,0} + a + b|} \quad (3)$$

where $C_{\text{COOCH}_3,0}$ refers to the concentration of carboxymethyl group at reaction time zero, and



Scheme 1

$$a = k(C_{EL,0} + C_{CH_3OH,0})/2(k' - k) \quad (4)$$

$$b = \left[\frac{k^2(C_{EL,0} + C_{CH_3OH,0})^2}{4(k' - k)^2} + \frac{kC_{EL,1}C_{CH_3OH,0}}{k' - k} \right]^{1/2} \quad (5)$$

By rearranging eq. (3), one gets

$$C_{COOCH_3} = \frac{a - b - (a + b)\exp[-2bk(1/K - 1)t + c]}{\exp[-2bk(1/K - 1)t + c] - 1} \quad (6)$$

where K refers to the equilibrium constant ($= k/k'$), and

$$c = \ln \frac{|C_{COOCH_3,0} + a - b|}{|C_{COOCH_3,0} + a + b|} \quad (7)$$

Eq. (6) implies that the values of two kinetic parameters, i.e., forward reaction rate constant k and equilibrium constant K , are required for calculating the time dependence of the concentration of the carboxymethyl end group ($CCOOCH_3$), as shown in Figure 6. The values of k and K were determined from the comparison of observed time dependence of $CCOOCH_3$, depicted in Figure 6, with eq. (6) by a nonlinear regression procedure. The values of K , k , and k' ($= k/K$) at 280, 290, and 300°C determined thus are listed in Table I. The

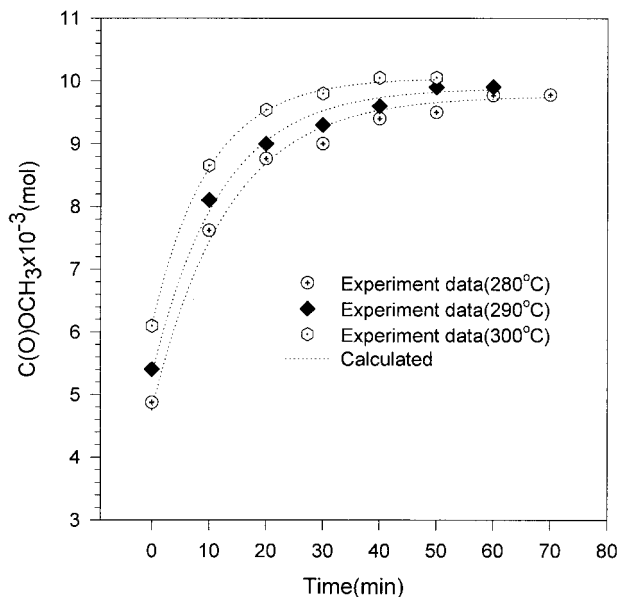


Figure 6 Time dependence of the concentration of $C(O)OCH_3$ in the depolymerization of PET by SC methanol for an initial charge ratio of methanol to PET of 10 and comparison with that calculated by eq. (6).

Table I Rate Parameters of Depolymerization of PET in Supercritical Methanol

	Temperature (°C)		
	280	290	300
Equilibrium constant $K(-)$	0.433	0.573	0.992
Standard error (%)	5.7	10.4	11.1
Forward reaction rate constant k [g-PET/(mol min)]	0.235	0.261	0.322
Standard error (%)	1.5	1.9	1.1
Reverse reaction rate constant k' [g-PET/(mol min)]	0.542	0.456	0.325

broken curves in Figure 6 represent the time dependencies of $CCOOCH_3$ calculated by eq. (6) with these estimates, and the experimental points fall on these calculated broken curves. It is concluded that eq. (6) can simulate the depolymerization process of PET in supercritical methanol.

Figure 7 indicates the temperature dependence of the rate constant in the depolymerization of PET in supercritical methanol (methanolysis of PET) for an initial charge ratio of methanol to PET of 10. The Arrhenius plot here yields the activation energy of 49.9 kJ/mol, close to a literature value⁴ (55.7 kJ/mol).

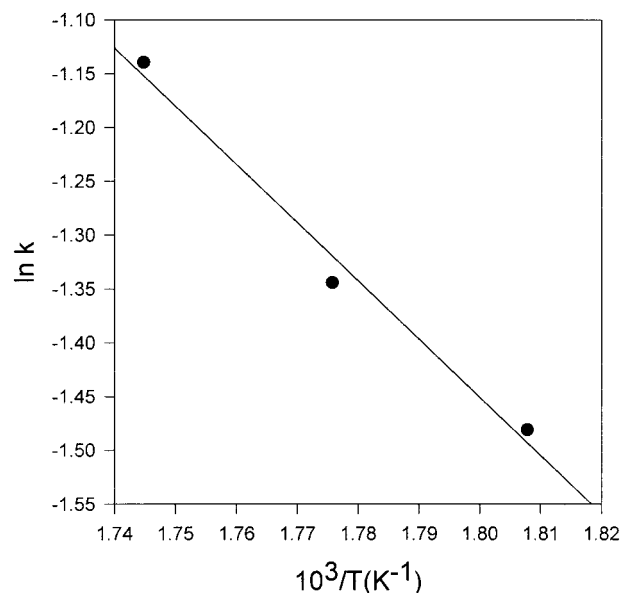


Figure 7 Arrhenius plot of rate constant of the depolymerization of PET by supercritical methanol for an initial charge ratio of methanol to PET of 10.

CONCLUSIONS

The depolymerization of PET in supercritical methanol was performed using a batch-type autoclave reactor. The conversion and the yield of DMT increased with rising temperature. After 60 min had passed, the polymerization reaction seemed to be equilibrated. The yield of DMT exceeded 50% above 280°C. The final yield of DMT at 300 and 310°C reached 97.0 and 97.7%, respectively. The yield of EG was slightly lower than that of DMT. The yield of DMT markedly increased with an increase in fluid density up to 0.08 g/cm³, equivalent to an initial charge ratio of 10 and a pressure of 8.26 MPa.

A kinetic model to simulate the depolymerization of PET in supercritical methanol was proposed, wherein the scission of one ester linkage in PET by a methanol molecule results in the formation of one carboxymethyl group and one hydroxyl group. The proposed model was constructed to describe the observed time dependence of carboxymethyl group concentration. The values of the forward reaction rate constant at 280, 290, and 300°C were determined by comparing the observed time dependence with that calculated by the proposed model. The activation energy was

evaluated to be 49.9 kJ/mol, a value close to a literature value (55.7 kJ/mol).

NOMENCLATURE

- C* concentration (mol/g-PET)
K equilibrium constant (–)
k forward reaction (methanolysis) rate constant [g-PET/(mol min)]
k' reverse reaction (polycondensation) rate constant [g-PET/(mol min)]
t time (s) or (min)

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