

# Depolymerization of Poly(trimethylene terephthalate) in Supercritical Methanol

Hao-Hong Zhang, Hong-Wei Xiang, Yong Yang, Yuan-Yuan Xu, Yong-Wang Li

State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan, Shanxi 030001, People's Republic of China

Received 2 September 2003; accepted 28 September 2003

**ABSTRACT:** The depolymerization of poly(trimethylene terephthalate) (PTT) in supercritical methanol was carried out with a batch-type autoclave reactor at temperatures ranging from 280 to 340°C, at pressures ranging from 2.0 to 14.0 MPa, and for reaction time of up to 60 min. PTT quantitatively decomposed into dimethyl terephthalate (DMT) and 1,3-propaniol (PDO) under the designed conditions. The yields of DMT and PDO greatly increased as the temperature rose. The yields of the monomers markedly increased as the pressure increased to 10.0 MPa, and they leveled off at higher pressures. The final yield of DMT at 320°C and 10.0

MPa reached 98.2%, which was much closer to the extent of the complete reaction. A kinetic model was used to describe the depolymerization reaction, and it fit the experimental data well. The dependence of the forward rate constant on the reaction temperature was correlated with an Arrhenius plot, which gave an activation energy of 56.8 kJ/mol. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 2363–2368, 2004

**Key words:** poly(trimethylene terephthalate) (PTT); depolymerization; supercritical methanol

## INTRODUCTION

Poly(trimethylene terephthalate) (PTT), a linear aromatic polyester made through the polycondensation of trimethylene glycol with terephthalic acid or dimethyl terephthalate (DMT), has recently become one of the most important polymer materials. PTT has an odd number of methylene units between the terephthalates moieties in its chemical structure in comparison with two common homologous polyesters, poly(ethylene terephthalate) (PET) and poly(1,4-butylene terephthalate) (PBT), and its molecule takes on an extended zigzag shape. Because of this special structure, PTT has outstanding resiliency, chemical resistance, and good thermal properties for fibers and engineering thermoplastics.<sup>1–3</sup>

The recovery of valuable products through the chemical recycling of polymers has been attracting attention in recent years for both environmental and economic reasons.<sup>4–12</sup> In particular, supercritical fluids, such as supercritical methanol (critical temperature = 239.4°C and critical pressure = 8.09 MPa), are very interesting for the quantitative recovery of monomers without a catalyst in a short time because they have higher diffusivity than liquids and higher solu-

bility than gases.<sup>13–17</sup> Yang et al.<sup>16</sup> reported that depolymerization in supercritical methanol produced two monomers, DMT and ethylene glycol, with almost a 100% yield in 40 min without a catalyst, and they found that both the yield of DMT and the degree of PET depolymerization were greatly effected by the temperature and reaction time. Shibata et al.<sup>17</sup> reported that the depolymerization of PBT in high-temperature and high-pressure methanol was an effective method for the quantitative recovery of DMT and 1,4-butanediol. A number of studies on PTT have been published.<sup>18–23</sup> However, little work has been performed on the depolymerization of PTT in supercritical methanol.

In this study, we investigated the possibility of the degradation of PTT to its monomers in supercritical methanol. All the experiments were performed with a batch-type reactor. The effects of the reaction temperature, pressure, and time on the yields of the monomers were researched, and a kinetic model was used to describe the reaction.

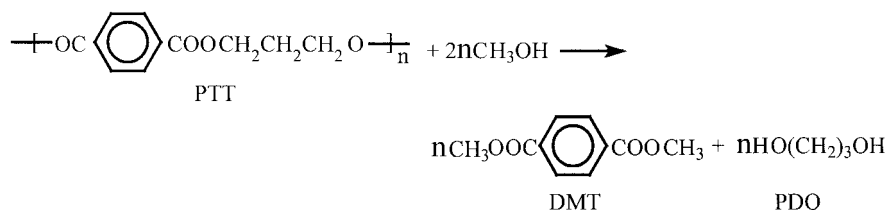
## EXPERIMENTAL

### Materials

The PTT samples were pure granules ( $\Phi 2 \times 3$  mm), instead of waste, and were provided by World Best Radici Co. (Changzhou, China). The intrinsic viscosity ( $[\eta]$ ) of PTT in a 60 : 40 (w/w) phenol/1,1,2,2-tetrachloroethane solution at 30°C was 0.95 dL/g, corresponding to a viscosity-average molecular weight

Correspondence to: H.-W. Xiang (hwxiang@sxicc.ac.cn).

Contract grant sponsor: National Natural Science Foundation of the People's Republic of China; contract grant number: 20176063.



**Scheme 1** Depolymerization of PTT in supercritical methanol.

( $M_v$ ) of 51,000, which was calculated with the Mark-Houwink equation ( $[\eta] = 0.000536 \times M_v^{0.69}$ ).<sup>24</sup> The resins melted at 210–240°C, as determined by differential scanning calorimetry at a heating rate of 10°C/min. Analytical-grade methanol and tetrahydrofuran (THF) were bought from Tianjin Chemical Reagent Co. (Tianjin, China) and used after further purification by distillation. A standard sample of DMT (>99%) was obtained from Aldrich (Milwaukee, WI). A standard sample of 1,3-propaniol (PDO;  $\geq 99.0\%$ ) was obtained from Shanghai Chemical Reagent Co. (Shanghai, China).

### Depolymerization

The reactor used for the methanolysis experiments, manufactured by Weihai Chemical Device Co. (Shandong, China), was made of stainless steel 316 and had a volume of 150 mL; it was fitted with a stirrer, a thermometer, and nitrogen inlet and outlet valves. Its maximum attainable temperature and pressure were 400°C and 25 MPa, respectively. The temperatures of the reactor and furnace were measured with K-type thermocouples, and the accuracy of the measured temperature was  $\pm 1.0^\circ\text{C}$ .

For all the experiments, a 10 : 1 (w/w) mixture of methanol and PTT was charged into the reactor at room temperature, and the air in the reactor was replaced with  $\text{N}_2$  gas to avoid the oxidation of PTT. Then, the reactor was heated directly to the specified temperatures as quickly as possible. After the required time under the designed reaction conditions, the vessel was removed from the heating collar and was quenched as soon as possible in ice water. The temperature of the reaction mixtures dropped to under 100°C within 1 min of quenching. After the reactor vessel was cooled to about 25°C, it was opened, and the products in the reactor were then taken out with a certain amount of cold methanol ( $< 10^\circ\text{C}$ ). The mixture was subsequently separated into solid and liquid phases by filtration. The contents of PDO and methanol in the filtrate were directly analyzed by gas chromatography (GC). The solid products, mainly composed of DMT and oligomers, were then dried at 50°C to a constant weight for gel permeation chromatography (GPC) analysis. The recoveries of DMT and PDO

were defined as percentages of the amounts of DMT and PDO calculated from GPC and GC data against the theoretical amounts of DMT and PDO when the PTT feed was completely depolymerized. Scheme 1 shows the depolymerization of PTT in supercritical methanol.

### Characterization

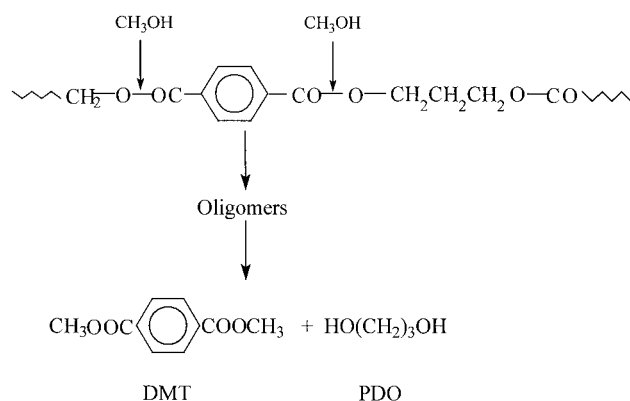
GC analysis was carried out on an SP-520 (Tengzhou Analyzer Co., Shandong, China) instrument fitted with a 2-m stainless column packed with Poropak-Q. The components were carried by a nitrogen flow and detected with a flame ionization detector. The temperatures of the column, detector, and injector port were 160, 180, and 180°C, respectively. The volume of the injected sample was 0.6  $\mu\text{L}$ .

GPC analysis was performed with a Shimadzu LC-3A high-performance liquid chromatograph equipped with a GPC-801 column (Kyoto, Japan). THF was used as a mobile phase at a pressure of 17 kgf/cm<sup>2</sup>, and the flow rate was 0.9 mL/min. The detector was an ultraviolet detector set at 254 nm. Polystyrene standards with a low polydispersity were used to generate a calibration curve for the molecular weight determination.

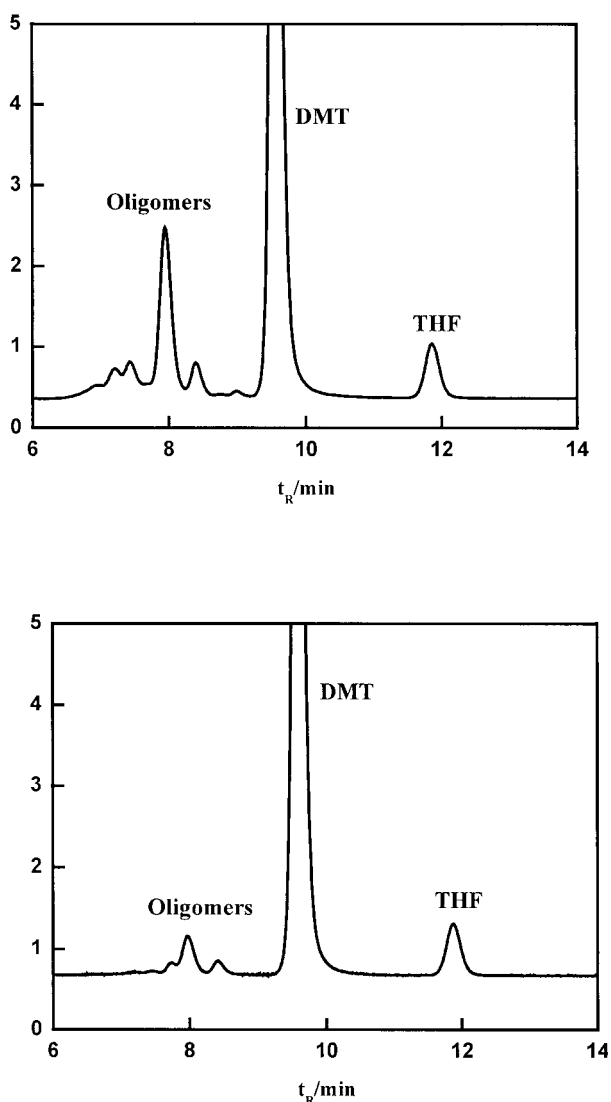
## RESULTS AND DISCUSSION

### Analysis of the solid products

In supercritical methanol, PTT was decomposed to the monomers DMT and PDO, low-molecular-weight oli-



**Scheme 2** Decomposition of PTT in supercritical methanol.



**Figure 1** GPC charts of the solid products obtained from the depolymerization of PTT at 320°C and 10.0 MPa for (a) 10 and (b) 30 min.

gomers and higher linear oligomers defined as THF-insoluble. Scheme 2 shows the pathway of the methanolysis of PTT with supercritical methanol, which is like the degradation of PET in supercritical methanol.<sup>25</sup>

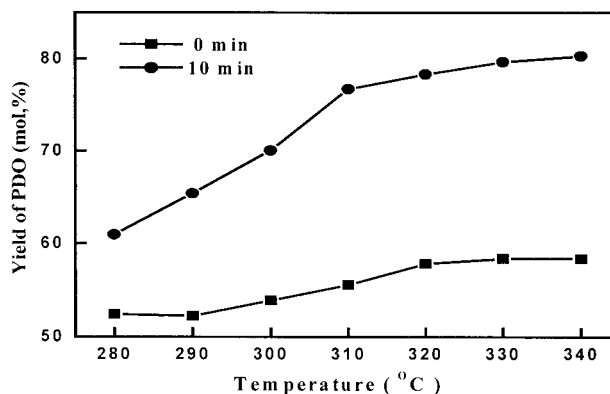
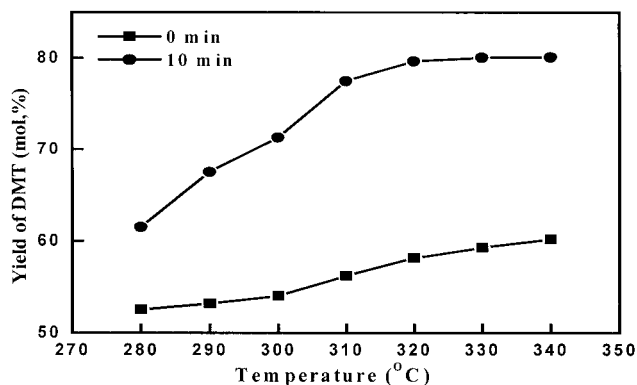
Figure 1(a,b) shows that the composites of DMT and oligomers in the solid products could completely be separated and detected accurately with the GPC method. In either case, the molecular weights of the oligomer peaks were evaluated to be about 300–500, suggesting that the components were oligomers containing 2–4 monomer units.

#### Effects of the reaction parameters

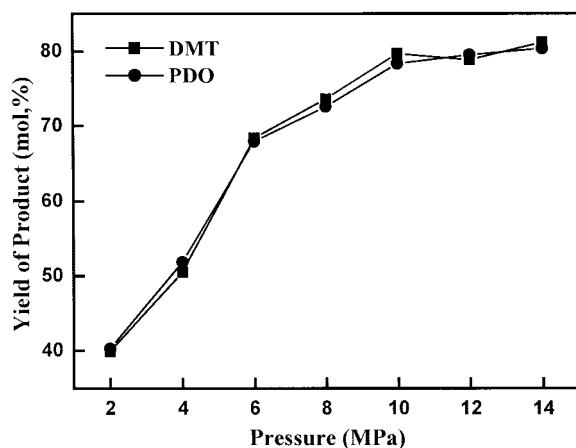
To study the influence of the reaction temperature on the yields of DMT and PDO, we performed the exper-

iments at a pressure of 10.0 MPa for 10 min. Because approximately 25 min was required for the prescribed conditions to be reached (this was defined as reaction time zero), significant yields of the monomers at reaction time zero were observed (Fig. 2). Both DMT and PDO were quantitatively recovered, and the formation of 1 mol of DMT resulted in the formation of the same amount of PDO. At reaction time zero, the yields of the monomers increased slowly as the temperature increased. However, at a reaction time of 10 min, the yields of the monomers sharply increased with an increase in the reaction temperature up to 320°C. Above this value, the yields increased mildly. Thus, all the experiments were performed above 320°C.

Figure 3 shows the effect of the reaction pressure on the yields of the monomers around the critical point of methanol. A series of experiments with different reaction pressures (2.0–14.0 MPa) were carried out at 320°C for 10 min. The yields of the monomers increased as the pressure increased, and they leveled off above 10.0 MPa. It may be that the solvent density was high under the supercritical state, being nearly the same order of magnitude as that of a typical organic liquid, and this gave the solvent a high capacity for the



**Figure 2** Temperature dependence of the yields of the monomers at 10.0 MPa with a 10 : 1 weight ratio of methanol to PTT.



**Figure 3** Pressure dependence of the yields of the monomers at 320°C for 10 min with a 10 : 1 weight ratio of methanol to PTT.

solute. At higher pressures, the supercritical fluid (SCF) densities were relatively insensitive to changes in the pressure.<sup>26,27</sup> For this reaction system, methanol had a higher capacity for dissolving liquidlike PTT under the supercritical methanol conditions than normal liquid methanol. The active ester linkages in PTT could be well dispersed in the methanol, and this facilitated the depolymerization. When the reaction pressure was greater than 10.0 MPa, the density of methanol became insensitive to the pressure. However, the activation volumes of the reaction in dilute fluids, which could increase the reaction rate constant significantly, were approximately  $\pm 1000 \text{ cm}^3/\text{mol}$  near the critical points, whereas they were between  $-50$  and  $30 \text{ cm}^3/\text{mol}$  in the liquid phase. The activation volumes were not constant but varied with both the pressure and temperature. As we moved away from the critical point, the activation volumes approached their liquid-phase values.<sup>28</sup> Therefore, as the pressure increased, the activation volumes also increased, and the yields of the monomers increased rapidly. However, a further increase in the pressure above the critical pressure of the solvent led to a reduction of the activation volumes, and the yields of the monomers approached constant values.

The effect of the reaction time on the depolymerization is depicted in Figure 4; the experiments were carried out at 10.0 MPa and 280–340°C for times of 0–60 min. The yields of DMT and PDO were notably enhanced as the time increased in all cases. The yield of DMT at 320°C reached 97.6 and 98.2% with reaction times of 30 and 60 min, respectively; these values were much closer to the extent of complete depolymerization. The yield of PDO was similar to that of DMT. PTT would apparently be decomposed completely at 320°C and 10.0 MPa after 30 min or more.

### Kinetic model

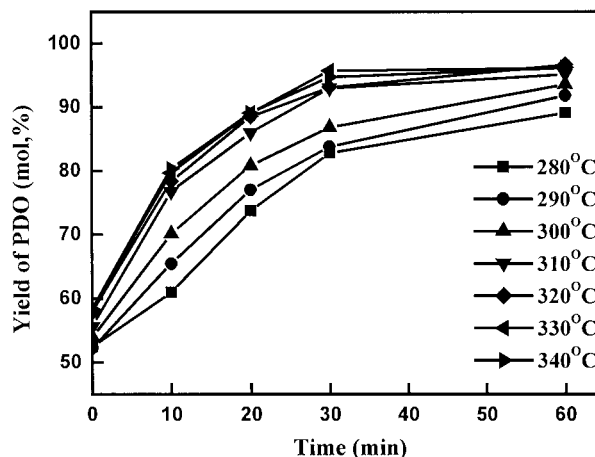
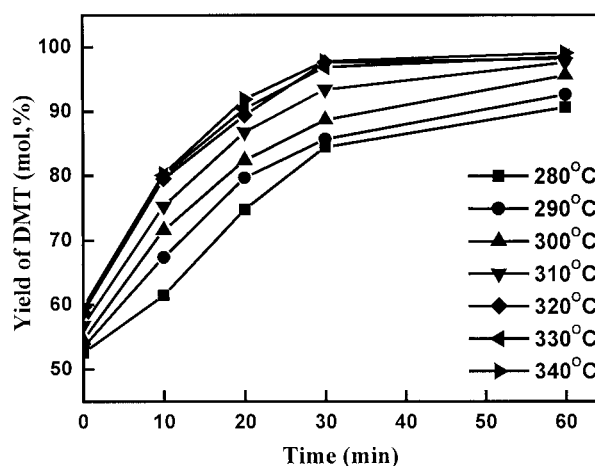
In kinetic studies of the depolymerization of PET with water and supercritical methanol, Campanelli et al.<sup>29</sup> and Kim et al.<sup>15</sup> used a second-order model.

On the basis of a similar concept, a kinetic model was proposed to describe the depolymerization of PTT in supercritical methanol. As shown in Scheme 2, the scission of two ester linkages by two methanol molecules forms two carboxymethyl groups ( $-\text{COOCH}_3$ ) in DMT and two hydroxyl groups ( $-\text{OH}$ ) in PDO.

Therefore, the second-order model can be expressed as follows:

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

where  $C_{\text{COOCH}_3}$  is the carboxymethyl group concentration;  $C_{\text{EL}}$  refers to the concentration of ester linkages;  $C_{\text{CH}_3\text{OH}}$  represents the concentration of  $\text{CH}_3\text{OH}$ ;



**Figure 4** Time dependence of the yields of the monomers at different temperatures and at 10 MPa with a 10 : 1 weight ratio of methanol to PTT.

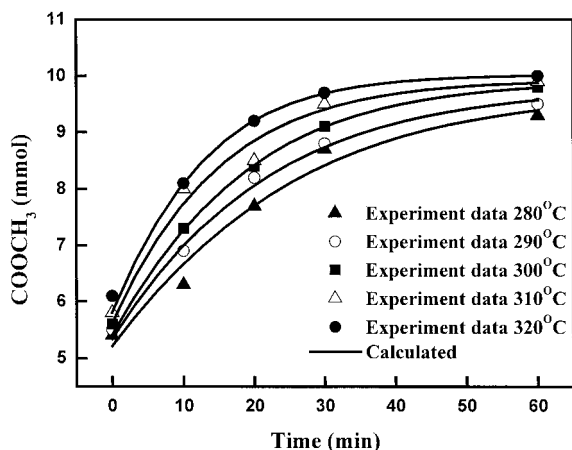


Figure 5 Kinetic plots by the second-order model for the reaction at different temperatures.

and  $k$  and  $k'$  denote the rate constants for forward and reverse reactions, respectively.

With respect to the stoichiometry, we find the following:  $C_{\text{COOCH}_3} = C_{\text{OH}}$ ,  $C_{\text{EL}} = C_{\text{EL},i} - C_{\text{COOCH}_3}$ , and  $C_{\text{CH}_3\text{OH}} = C_{\text{CH}_3\text{OH},i} - C_{\text{COOCH}_3}$ . Then, eq. (1) can be reduced to

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

where subscript  $i$  indicates the initial charge concentration.

The integration of eq. (2) gives the following equation:

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

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

$$A = -k(C_{\text{EL},i} + C_{\text{CH}_3\text{OH},i})/2(k - k') \quad (4)$$

$$B = [A^2 - k C_{\text{EL},i} C_{\text{CH}_3\text{OH},i}/(k - k')]^{1/2} \quad (5)$$

$$M = \ln \frac{|C_{\text{COOCH}_3,0} + A - B|}{|C_{\text{COOCH}_3,0} + A + B|} \quad (6)$$

The rearrangement of eq. (3) leads to the following form:

TABLE I  
Rate Parameters of the Depolymerization of PTT in Supercritical Methanol

	Temperature (°C)				
	280	290	300	310	320
$k$ (g of PTT mol <sup>-1</sup> min <sup>-1</sup> )	0.1128	0.1262	0.1637	0.2154	0.2449
$k'$ (g of PTT mol <sup>-1</sup> min <sup>-1</sup> )	0.1668	0.1739	0.2017	0.2275	0.2474
$K_e$	0.6763	0.7257	0.8116	0.9468	0.9899

$$C_{\text{COOCH}_3} = \frac{(A - B) - (A + B) \exp[2B(k - k')t + M]}{\exp[2B(k - k')t + M] - 1} \quad (7)$$

where  $A$  and  $B$  are constants for specific reaction conditions. The rate constants of methanolysis,  $k$  and  $k'$ , were estimated through the fitting of experimental data to eq. (7).

Figure 5 shows the plots of  $C_{\text{COOCH}_3}$  against time at different reaction temperatures. The values of  $k$ ,  $k'$ , and the equilibrium constant ( $K_e = k/k'$ ) in the reaction temperature range of 280–320°C were determined by the proposed model and are listed in Table I. The curves in Figure 5 represent the time dependence of  $C_{\text{COOCH}_3}$  calculated by eq. (7), and the experimental data were found to fit the kinetic model well. The second-order model could simulate the depolymerization of PTT in supercritical methanol.

The temperature dependence of  $k$  can be expressed as follows:

$$\ln k = \ln A - E_a/RT \quad (8)$$

where  $E_a$  is the activation energy,  $A$  is the frequency factor,  $R$  is the gas constant, and  $T$  is the temperature.

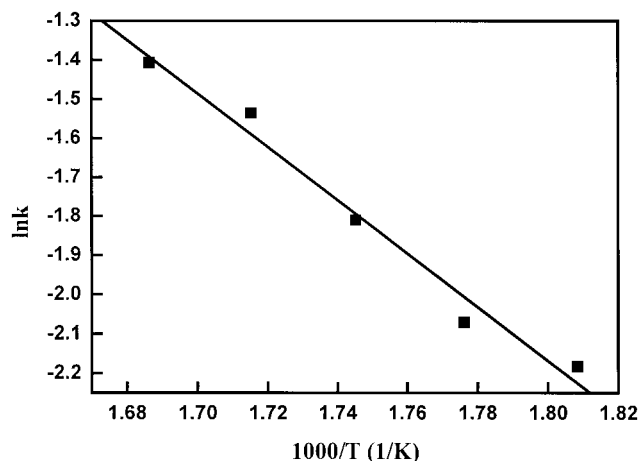


Figure 6 Arrhenius plot for the depolymerization of PTT in supercritical methanol.

TABLE II  
Variation of  $K_e$ ,  $\Delta G$ ,  $\Delta H$ , and  $\Delta S$   
with the Temperature ( $T$ )

$T$ (K)	$K_e$	$\Delta G$ (J/mol)	$\Delta H$ (J/mol)	$\Delta S$ (J/k/mol)
553	0.6763	1799.5	—	—
563	0.7257	1501.8	-18,261.9	-35.1
573	0.8116	995.2	-24,039.7	-43.6
583	0.9468	265.2	-42,824.6	-73.9
593	0.9899	50.1	-28,072.0	-47.4

Plots of  $\ln k$  against  $1000/T$  in the reaction are shown in Figure 6. The  $E_a$  value calculated from these plots was 56.8 kJ/mol.

The effects of the temperature on the  $K_e$ , Gibbs free energy ( $\Delta G$ ), enthalpy ( $\Delta H$ ), and entropy ( $\Delta S$ ) values for the reaction are shown in Table II.

### CONCLUSIONS

The depolymerization of PTT was carried out in supercritical methanol at different temperatures and pressures and for different reaction times. The yields of DMT and PDO greatly increased as the temperature increased. The yields of the monomers also sharply increased as the pressure increased, but they approached constant values above 10.0 MPa. PTT seemed to completely depolymerize to monomers at 320°C after 30 min or more. The final yields of DMT and PDO at 320°C and 10.0 MPa with a 10 : 1 weight ratio of methanol to PTT reached 98.2%.

A kinetic model was proposed to simulate the depolymerization of PTT in supercritical methanol, in which the scission of one ester linkage in PTT by a methanol molecule resulted in the formation of one carboxymethyl group and one hydroxyl group. The experimental data showed good agreement with the model.  $E_a$ , as estimated from an Arrhenius plot, was 56.8 kJ/mol.

The authors thank Chih-Yu Kao, Ben-Zu Wan, and S. Mishra for their help.

### References

- Desboroughm, I. J.; Hall, I. H.; Neisser, J. Z. *Polymer* 1979, 20, 545.
- Kim, J. H.; Lee, J. J.; Yoon, J. Y.; Lyoo, W. S.; Kitek, R. *J Appl Polym Sci* 2001, 82, 99.
- Beshouri, S. M.; Brown, H. H.; Chuah, K.; Dangayach, K.; How, C. C. *Polym Prepr* 1999, 40(1), 569.
- Kurokawa, H.; Ohshima, M.; Sugiyama, K.; Miura, H. *Polym Degrad Stab* 2003, 79, 529.
- Mishra, S.; Goje, A. S. *Polym Int* 2003, 52, 337.
- Mansour, S. H.; Ikladious, N. E. *Polym Test* 2002, 21, 497.
- Wan, B.-Z.; Kao, C.-Y.; Cheng, W.-H. *Ind Eng Chem Res* 2001, 40, 509.
- Kao, C.-Y.; Wan, B.-Z.; Cheng, W.-H. *Ind Eng Chem Res* 1998, 37, 1228.
- Yamaye, M.; Hashime, T.; Yamamoto, K.; Kosugi, Y.; Cho, N.; Ichiki, T. *Ind Eng Chem Res* 2002, 41, 3993.
- Goje, A. S.; Mishra, S. *Macromol Mater Eng* 2003, 288, 326.
- Kao, C. Y.; Cheng, W. H.; Wan, B. Z. *J Appl Polym Sci* 1998, 70, 1939.
- MacDonald, W. A. *Polym Int* 2002, 51, 923.
- Sako, T.; Sugeta, T.; Otake, K.; Yoda, S.; Takebayashi, Y.; Okajima, I.; Kamizawa, C. *Polym J* 1999, 31, 714.
- Sako, T.; Okajima, I.; Sugeta, T.; Otake, K.; Yoda, S.; Takebayashi, Y.; Kamizawa, C. *Polym J* 2000, 32, 178.
- Kim, B. K.; Hwang, G. C.; Bae, S. Y.; Yi, S. C.; Kumazawa, H. *J Appl Polym Sci* 2001, 81, 2102.
- Yang, Y.; Lu, Y. J.; Xiang, H. W.; Xu, Y. Y.; Li, Y. W. *Polym Degrad Stab* 2002, 75, 185.
- Shibata, M.; Masuda, T.; Yosomiya, R.; Meng, L. H. *J Appl Polym Sci* 2000, 77, 3228.
- Huang, J. M.; Chang, F. C. *J Polym Sci Part B: Polym Phys* 2000, 38, 934.
- Pyda, M.; Boller, A.; Grebowicz, J.; Chuan, H.; Lebedev, B. V.; Winderlich, B. *J Polym Sci Part B: Polym Phys* 1998, 36, 2499.
- Ramiro, J.; Eguiazabal, J. I.; Nazabal, J. *J Appl Polym Sci* 2002, 86, 2755.
- Wang, X. S.; Li, X. G.; Yan, D. Y. *Polym Degrad Stab* 2000, 69, 361.
- Chung, W. T.; Yeh, W. J. *J Appl Polym Sci* 2002, 83, 2426.
- Hong, P. D.; Chung, W. T.; Hsu, C. F. *Polymer* 2002, 43, 3335.
- Chuah, H. H.; Lin-Vien, D.; Soni, U. *Polymer* 2001, 42, 7137.
- Goto, M.; Koyamotom, H.; Kodama, A.; Hirose, T.; Nagaoka, S.; McCoy, B. J. *AIChE J* 2002, 48, 136.
- Tucker, S. C. *Chem Rev* 1999, 99, 391.
- Kirby, C. F.; McHugh, M. A. *Chem Rev* 1999, 99, 565.
- Savage, P. E.; Gopalan, S.; Mizan, T. I.; Martino, C. J.; Brock, E. E. *AIChE J* 1995, 41, 1723.
- Campanelli, J. R.; Cooper, D. G.; Kamal, M. R. *J Appl Polym Sci* 1994, 53, 985.