

Depolymerization of Poly(butylene terephthalate) Using High-Temperature and High-Pressure Methanol

MITSUHIRO SHIBATA,¹ TAIJI MASUDA,¹ RYUTOKU YOSOMIYA,¹ MENG LING-HUI²

¹ Department of Industrial Chemistry, Chiba Institute of Technology, 2-17-1, Tsudanuma, Narashino, Chiba 275-0016, Japan

² Department of Applied Chemistry, Harbin Institute of Technology, Harbin 150001, China

Received 22 July 1999; accepted 28 January 2000

ABSTRACT: Poly(butylene terephthalate) (PBT) was depolymerized in excess methanol at high-temperature (473–523 K) and high-pressure (4–14 MPa) conditions. Considering the critical point of methanol (512.6 K, 8.09 MPa), the reaction pressure was varied over the range of 6–14 MPa at the reaction temperature of 513 K. As a result, ca. 20 min was required to recover dimethyl terephthalate and 1,4-butanediol, quantitatively, at any pressure, indicating that the supercritical state of methanol is not a key factor of degradation of PBT and that the effect of pressure is little. On the contrary, when the reaction temperature was varied over the range of 473–523 K at the pressure 12 MPa, the decomposition rate constant of PBT at the reaction temperatures (503–523 K) higher than the melting temperature of PBT (500 K) was much higher than that at 473–483 K. This result indicates that melting of PBT is an important factor for the short-time depolymerization of PBT. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 3228–3233, 2000

Key words: poly(butylene terephthalate); depolymerization; methanolysis; supercritical fluid; kinetic study

INTRODUCTION

Recovery of valuable products by the chemical recycling of waste plastics has been attracting attention in recent years for both environmental and economic reasons.^{1,2} The depolymerization of poly(ethylene terephthalate) (PET)^{3–6} by hydrolysis, methanolysis, and glycolysis has been actively investigated as a method of the chemical recycling of mainly a large quantity of waste PET bottles. Especially, the depolymerization by high-temperature and high-pressure water and methanol containing supercritical fluids^{4–6} has been attracting greater attention in recent years as a

method of quantitative recovery of monomers without catalyst in a short time. Arai and coworkers reported that PET can be smoothly depolymerized in the supercritical water of 673 K, 40 MPa, and terephthalic acid and ethylene glycol were recovered in ca. 90 and 10% yields, respectively, at the reaction time 12.5 min.⁴ The low recovery of ethylene glycol is thought to be attributed to the decomposition of the formed ethylene glycol by the action of terephthalic acid as an acid catalyst. Also, Sako et al. reported that both dimethyl terephthalate (DMT) and ethylene glycol can be almost quantitatively recovered by the depolymerization of PET in the supercritical methanol of 573 K, 10 MPa for 30 min.^{5,6} However, little work on the depolymerization of other popular polyesters than PET in a similar manner has been done. In the present article, the depolymer-

Correspondence to: M. Shibata.

Journal of Applied Polymer Science, Vol. 77, 3228–3233 (2000)
© 2000 John Wiley & Sons, Inc.

ization of poly(butylene terephthalate) (PBT) in excess methanol is studied by using a high-temperature and high-pressure batch reactor. Our attention is given to the kinetics around a critical point of methanol and around the melting temperature (T_m) of PBT.

EXPERIMENTAL

Materials

The PBT used was TRB-J [rectangular granules, melt flow rate 22 g/10 min at 235°C and a load of 2160 g, number-average molecular weight (\bar{M}_n) 29,700] manufactured by Teijin Co. Ltd., Tokyo, Japan. The reagent grade methanol, DMT, and 1,4-butanediol (BTD) (Kanto Chemicals Co. Ltd., Tokyo, Japan) were used without further purification.

Depolymerization

A 50-mL stainless steel (SUS 304) autoclave equipped with pressure gauge was used for the following methanolysis experiments. All the reactions were performed without stirring. In case of the reaction condition, 513 K, 6 MPa, PBT 0.65 g, and methanol 9.10 mL were added to the autoclave and the mixture was heated to 513 K with a mantle heater. Approximately 25 min was required until the prescribed condition (513 K, 6 MPa) was reached. After a specified time interval (0–80 min) at the reaction temperature and pressure, the autoclave was removed from the mantle heater and quenched quickly in an ice bath. The temperature of the reaction mixture dropped to under 100°C within a minute of quenching. After the reaction vessel was cooled to about 25°C and opened, methanol was added to solubilize the precipitated DMT. After quenching in the early stage of the reaction, the powder of unreacted PBT was dispersed in the methanol solution. The unreacted PBT was filtered by using a sintered glass filter and dried at 80°C *in vacuo*. The methanol solution was analyzed by gas chromatography (GC) and gel permeation chromatography (GPC). The recoveries of DMT and BTD are defined as percentages of the DMT and BTD amounts contained in the methanol solution calculated from the gas chromatographic data against the theoretical DMT and BTD amounts in case that the feed PBT was completely depolymerized, respectively. In the experiments at another reaction

temperature (523, 503, 483, 473 K) and pressure (6–14 MPa), the quantity of PBT and methanol was changed at a constant ratio of PBT/methanol (0.65 g/9.10 mL).

Also, the following experiment was performed to recover the crystalline DMT. PBT 3.80 g and methanol 53.2 mL were added to a 89-mL stainless autoclave. The mixture was depolymerized at 523 K, 6 MPa for 20 min in a similar manner (ca. 30 min was required until the prescribed condition was reached). After the vessel was cooled to 0°C, the precipitated crystals were filtered. The reaction vessel was washed three times with a slight amount of cold methanol. The obtained crystals were washed with the cold methanol and dried at 50°C *in vacuo* for 3 h to give almost pure DMT 2.91 g (mp. 145°C; reagent of DMT: mp. 146°C) in 86% recovery. The IR spectrum of the obtained DMT substantially coincided with that of the reagent DMT. The liquid phase contained BTD and small amounts of DMT and PBT oligomers, as is revealed from the GC and GPC data.

Characterization

IR spectra of the obtained solids were measured on a FTIR 8100 spectrometer (Shimadzu Co. Ltd., Japan) by KBr method. Gas chromatographic analyses were carried out on a Shimadzu GC-8A instrument (detector TCD), fitted with a glass column (3.2 mm, 2.0 m) packed with Thermon-3000 Shincarbon A (Shimadzu Co. Ltd.), using helium as a carrier gas. The injection temperature was 250°C; the column was heated from 100 to 250°C at a heating rate of 10°C/min. Ethylene glycol was used as an internal standard for the determination of monomer recovery. GPC analysis was performed by using a Shimadzu LC-9A instrument equipped with two linear PLgel 5- μ m Mixed-D columns (linear range of molecular weight: 200–400,000; Polymer Laboratories Ltd.) by using tetrahydrofuran as the eluant at a pressure of 32 kgf/cm²; the elution rate was 0.5 mL/min and the detector was the refractive index type. Polystyrene standards with a low polydispersity were used to generate a calibration curve for the molecular weight determination.

RESULTS AND DISCUSSION

Effect of Pressure and Temperature on the Depolymerization of PBT

To investigate the change of depolymerization behavior of PBT in methanol around the critical

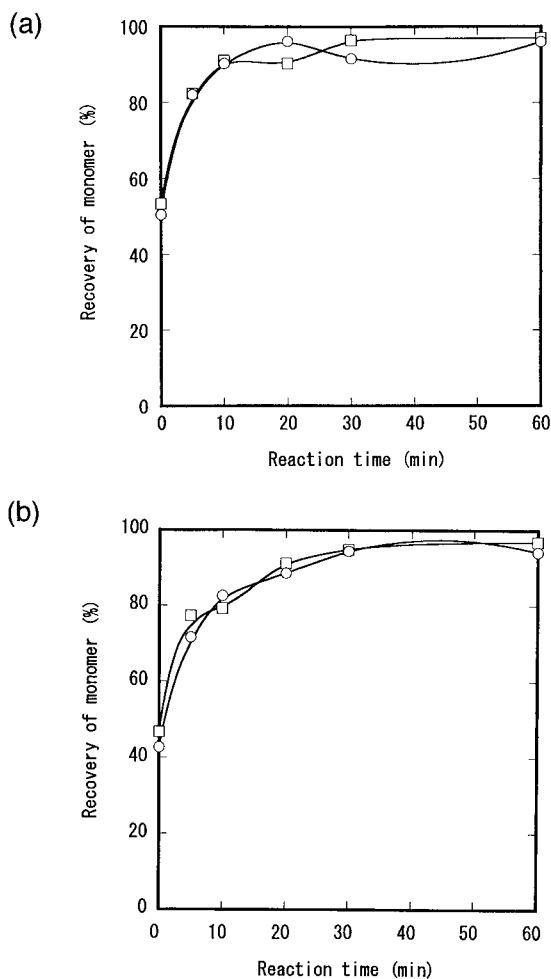


Figure 1 Effect of pressure on the depolymerization of PBT in methanol at temperature 513 K and pressure (a) 6 MPa and (b) 10 MPa. (□) DMT, (○) BTB.

point (512.6 K, 8.09 MPa), the reaction pressure was varied from 6 to 14 MPa at 513 K. About 20 min was required until the prescribed condition was reached and the time was defined as a reaction time 0. The typical time courses of recovery of DMT and BTB at 513 K, 6 MPa and 513 K, 10 MPa are shown in Figure 1. Regarding the condition 6 MPa, 513 K, recoveries of both monomers were ca. 50% at $t = 0$. The recoveries became ca. 90% at 10 min. Both monomers were quantitatively recovered at 20 min, considering the loss in posttreatment. Depolymerization at the pressure (8, 10, 12, 14 MPa) higher than 6 MPa showed almost similar time course [for example, Fig. 1(b)]. This result indicates that the supercritical state of methanol is not a key factor of degradation of PBT and that the effect of pressure is little.

Next, the reaction pressure was varied from 4 to 12 MPa at 483 K. In a similar manner to the

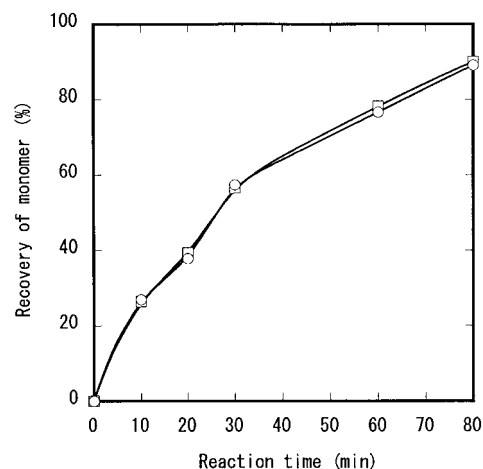


Figure 2 Time course of recovery of monomers for the depolymerization of PBT in methanol at 483 K, 6 MPa. (□) DMT, (○) BTB.

depolymerization at 513 K, there was little influence of pressure on the depolymerization behavior. The typical time course of recoveries of DMT and BTB at 6 MPa, 483 K is shown in Figure 2. In this case, over 80 min was required for the completion of depolymerization. It is obvious from the comparison with Figure 1 that it takes much longer to complete the depolymerization at 483 K than at 513 K.

GPC analyses of the samples prepared by the vacuum evaporation (80°C, 20 Torr) of the liquid

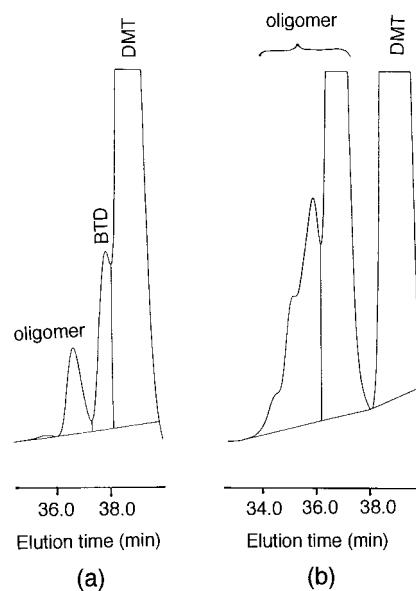


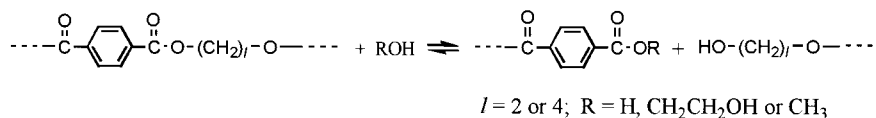
Figure 3 GPC charts of the concentrated liquid phase obtained by the depolymerization of PBT for 30 min at (a) 513 K, 10 MPa and (b) 483 K, 10 MPa.

phase in which the precipitated DMT was removed by filtration were performed to evaluate the molecular weight of the PBT oligomer contained in the solution. The GPC chart does not reflect the amount of BTB because a considerable amount of BTB is removed in the evaporation. Figure 3(a,b) shows the GPC charts of the samples depolymerized at 513 K, 10 MPa and 483 K, 10 MPa, respectively, for 30 min. Regarding the condition 513 K, 10 MPa, the molecular weights of the two oligomer peaks are evaluated to be about 300–500, suggesting that the two components are the oligomers containing 2–4 monomer units. The amounts of the oligomers were very small relative to that of DMT solubilized to methanol. Regarding the condition, 483 K, 10 MPa, the amounts of the oligomers increased and the peaks of oligomers with higher molecular weights were ob-

served, corresponding to the lowering of the reaction temperature. In either condition, the oligomers soluble to methanol have very low molecular weights.

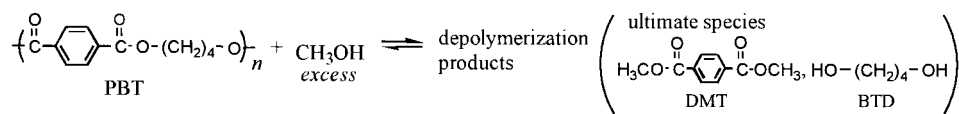
Kinetic Study of the Depolymerization of PBT

Kinetic study of the depolymerization of PBT was carried out to investigate the effect of temperature in detail. Campanelli et al.^{7,8} and Chen and Chen⁹ reported the kinetic analyses on the basis of the change of concentration of carboxylic acids and ethylene glycol by the reaction of ester group of PET with water and ethylene glycol in the hydrolysis and glycolysis of PET, respectively. In the case of methanolysis of PBT, the quantitative analysis of carbomethoxy group and highly volatile methanol are very difficult:



Also, the quantitative analysis of each oligomer formed by the stepwise depolymerization of PBT is difficult. Therefore, we performed the kinetic study regarding the disappearance rate of PBT in the case that unreacted PBT is present at a relatively short reaction time in a similar manner to the kinetic study of methanolysis of PET.⁶ The depolymerization condition for the kinetic study is as follows: temperatures 473, 483, 503, 513, 523

K, pressure 12 MPa, and reaction time 0–20 min. Although we tried the depolymerization at 493 K near T_m of PBT, it was very difficult to attain the constant pressure and temperature. Because an excess amount of methanol is used in this reaction, the reaction is regarded as obeying pseudo first-order kinetics. Therefore, the overall depolymerization reaction rate of PBT is expressed by:



$$-d[\text{PBT}]/dt = k[\text{PBT}] \quad (1)$$

where [PBT] means concentration of PBT, k is the reaction rate constant, and t is the reaction time. Integration of eq. (1) gives

$$\ln[\text{PBT}]_0/[\text{PBT}] = kt \quad (2)$$

where [PBT] is the residual PBT concentration at time t and $[\text{PBT}]_0$ is the PBT concentration at $t = 0$. Assuming that the volume of reaction phase is constant, the following is obtained:

$$\ln m_0/m = kt \quad (3)$$

where m_0 is not the weight of feed PBT but that of residual PBT at $t = 0$, because it takes ca. 20 min to attain the prescribed reaction condition ($t = 0$) in our experiment, and m is that of residual PBT at time t . For example, at the experimental condition of 513 K, 12 MPa, the relative amount of each component at $t = 0$ is approximately as follows: residual PBT, 22% of the feed PBT; recovery of monomer, 50%; oligomer with molecular weight < 2000, 28% as a converted value into the recovery of monomer when the oligomer is completely depolymerized.

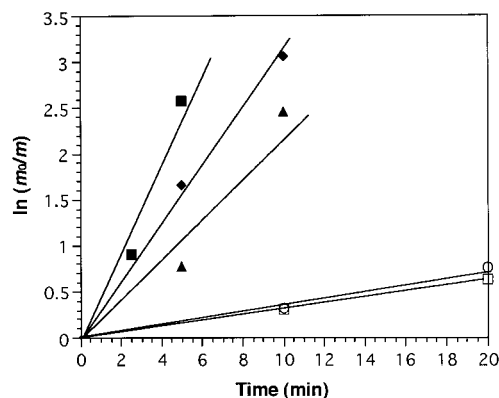


Figure 4 Relation between the decomposition ratio of PBT and reaction time. (■) 523 K, (◆) 513 K, (▲) 503 K, (○) 483 K, (□) 473 K.

The plots of $\ln m_0/m$ against t at various temperatures are shown in Figure 4. Although it is difficult to determine a precise value of k from the two experimental points, the approximate k was evaluated from the slope of a straight line through the origin (Table I). The k at the reaction temperatures 503–523 K is much larger than that at 473–483 K. Also, it is known that the temperature dependency of k is expressed by the equation:

$$\ln k = \ln A - E_a/RT \quad (4)$$

where E_a is the activation energy, A is the frequency factor, R is the gas constant, and T is temperature. The plots of $\ln k$ against $1000/T$ in this reaction are shown in Figure 5. It is obvious that the plot is jumping around the temperature (483–503 K), where is near T_m of PBT (500 K). A similar result is reported by Sako et al. for the depolymerization of PET in methanol.⁶ This result indicates that melting of PBT is an important factor for the short-time depolymerization of PBT. The molten PBT is thought to be partially miscible with methanol, as is shown by the experimental result that

Table I Reaction Rate Constants for PBT Decomposition at 12 MPa in Methanol

T (K)	k (min^{-1})
473	0.029
483	0.033
503	0.212
513	0.310
523	0.460

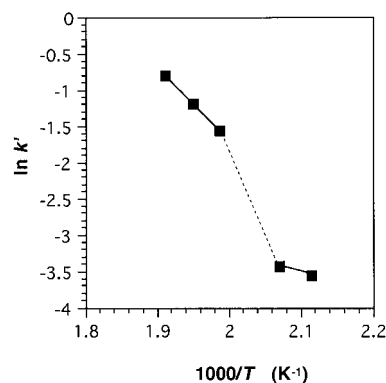


Figure 5 Arrhenius plot for PBT depolymerization in methanol.

the unreacted PBT changed from rectangular granules to powder dispersed in the methanol solution after quenching in the early stage of the reaction. The partial miscibility may enhance greatly the reactivity. The E_a calculated from the slope of the temperature region between 503 and 523 K is 84 kJ/mol, which is comparable to the E_a for the glycolysis of PET in molten state (92 kJ/mol).⁸ The E_a calculated from the slope of the temperature region between 473 and 483 K seems to be 25 kJ/mol by seems. The activation energy of depolymerization of PBT at 503–523 K is rather higher than that at 473–483 K. Higher temperature is needed more in the methanolysis of PET (573 K, 10 MPa)⁶ than in that of PBT (513 K, 6–14 MPa) to depolymerize completely within 30 min. The difference should be attributed to the higher T_m of PET (529 K) than PBT (500 K).

CONCLUSION

The depolymerization of PBT in high-temperature methanol was an effective method for the quantitative recovery of the corresponding monomers. Effect of the reaction pressure on the depolymerization rate was little, whereas that of temperature was very large for the experiments at the reaction conditions, 483 K, 4–12 MPa and 513 K, 6–14 MPa. In the former conditions, over 80 min was required for the completion of the depolymerization, and ca. 20 min in the latter conditions. Considering the critical point of methanol (512.6 K, 8.09 MPa), the special effect of supercritical methanol on the depolymerization rate was not observed. The kinetic study at the reaction conditions 473–523 K, 12 MPa revealed that the decomposition rate constant of PBT dramati-

cally increased when the reaction temperature is higher than the melting temperature of PBT (500 K). This result suggests that partial miscibility of the molten PBT and methanol is an important factor for the short-time depolymerization

REFERENCES

1. Leaversuch, R. D. *Mod Plast* 1991, 68, 40.
2. Scheiers, J. *Polymer Recycling*; Wiley Series in Polymer Science, 1998.
3. Paszun, D.; Spsychaj, T. *Ind Eng Chem Res* 1997, 36, 1373.
4. Adschiri, T.; Sato, O.; Machida, K.; Saito, N.; Arai, K. *Kagaku Kogaku Ronbunshu* 1997, 23, 505.
5. Sako, T.; Sugeta, T.; Otake, K.; Nakazawa, N.; Sato, M.; Namiki, K.; Tsugumi, M. *J Chem Eng, Jpn* 1997, 30, 342.
6. Sako, T.; Sugeta, T.; Otake, K.; Takebayashi, Y.; Kamizawa, C.; Tsugumi, M.; Hongo, M. *Kobunshi Ronbunshu* 1998, 55 (11), 685.
7. Campanelli, J. R.; Kamal, M. R.; Cooper, D. G. *J Appl Polym Sci* 1993, 48, 443.
8. Campanelli, J. R.; Kamal, M. R.; Cooper, D. G. *J Appl Polym Sci* 1994, 54, 1731.
9. Chen, J.-W.; Chen, L.-W. *J Appl Polym Sci* 1999, 73, 35.