

Alkaline Depolymerization of Poly(trimethylene terephthalate)

JOON HO KIM,¹ JOON JUNG LEE,¹ JI YOUNG YOON,^{1,*} WON SEOK LYOO,¹ RICHARD KOTEK²

¹ School of Textiles, Yeungnam University, 214-1 Daedong, Kyongsan 712-749, Korea

² Department of Textile Engineering, Chemistry and Science, North Carolina State University, Raleigh, North Carolina 27695

Received 2 October 2000; accepted 28 December 2000

ABSTRACT: The purpose of this study was to investigate the effects of reaction media, composition, and temperature on the rate of the alkaline depolymerization of poly(trimethylene terephthalate) (PTT). The alkaline depolymerization of PTT was carried out at 160–190°C in ethylene glycol (EG), diethylene glycol (DEG), triethylene glycol (TEG), ethylene glycol monobutyl ether (EGMBE), diethylene glycol monoethyl ether (DEGMEE), and a mixture of these solvents. During the reaction, PTT was quantitatively converted to disodium terephthalate and 1,3-propanediol. The alkaline depolymerization reaction rate constants were calculated based on the concentration of sodium carboxylate, which was equivalent to the molar amount of sodium hydroxide. The depolymerization rate of PTT was increased by increasing the reaction temperature and by adding ethereal solvents. Moreover, the depolymerization rate was significantly accelerated in the order of EG < DEG < TEG < EGMBE < DEGMEE. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 99–107, 2001

Key words: poly(trimethylene terephthalate) (PTT); alkaline depolymerization; rate constant; ethereal solvents

INTRODUCTION

Poly(trimethylene terephthalate) (PTT) is an alkyaryl polyester made by the polycondensation of trimethylene glycol with terephthalic acid (TPA) or dimethyl terephthalate. Although the polymer was first synthesized by Whinfield and Dickson in 1941, it was never commercialized because of the lack of an economical source of trimethylene glycol monomer. Recently, Shell Chemical Co. an-

nounced the development of technology to make trimethylene glycol economically via the hydroformylation of ethylene oxide. With a cheap monomer source, it is now possible to commercialize PTT at a competitive price.^{1–3}

PTT has an odd number of methylene units between the terephthalates moieties compared to poly(ethylene terephthalate) (PET) and poly(butylene terephthalate), which have even numbers of methylene units. PET molecules are more fully extended. Two carboxyl groups of each terephthaloyl group are situated in opposite directions. Also, all bonds are in the trans conformation, with successive phenylene groups at the same inclination along the chain.^{4–7} PTT differs from this conformation with bonds of the —O—(CH₂)₃—O— unit having the sequence trans–gauche–

Correspondence to: J. H. Kim (kimjnh@yu.ac.kr).

*Permanent address: Department of Textile Finishing, Textile Polytechnic College, Taegu 704-190, Korea.

Contract grant sponsor: Yeungnam University (year 2000); contract grant sponsor: Polyester Regional Research Center, Yeungnam University.

Journal of Applied Polymer Science, Vol. 82, 99–107 (2001)
© 2001 John Wiley & Sons, Inc.

gauche–trans, leading to the contraction of the repeating unit and, because of the opposite inclinations of successive phenylene groups along the chain, the molecule takes on an extended zigzag shape.^{8–11} Because of this chemical structure, PTT has special characteristics as a fiber. It is particularly interesting in carpet fibers, where it has shown outstanding resiliency and chemical resistance.^{12–16} Also, this polymer shows potential in the field of engineering thermoplastic polymers and fabrics. It is especially important to improve tactility of fabrics. Just like PET, PTT fabrics would require alkaline finishing to improve fabric softness. PTT is a relatively new polymeric material, and only limited information is available. Currently, the alkaline finishing of PTT fiber has not been reported.

Global commercial interest in PTT will expand capacity and end uses. An increase in the uses of PTT products will result in a greater amount of waste materials. In recent years, chemical recycling of waste polymers has mainly focused on obtaining valuable products from waste materials.^{17–19} High-quality TPA, which can be used for the synthesis of other polymer resins, can be obtained through the alkaline depolymerization of PTT.

In this study, we investigated the effects of reaction media, composition, and temperature on the rate of depolymerization of PTT based on studies of the alkaline depolymerization of PET.^{20–25} The results of this study confirmed that PTT waste can be successfully converted into useful products.

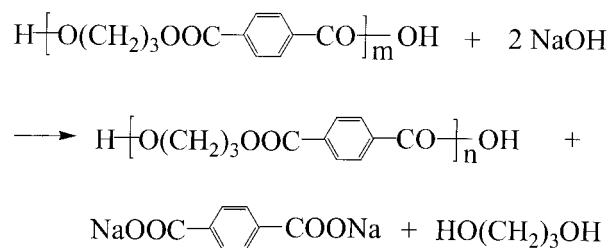
EXPERIMENTAL

Materials

Instead of PTT wastes, pure PTT chips (intrinsic viscosity (IV) = 0.92, Shell Co., Houston, TX) were used as the standard substrate. Commercially available reagent-grade sodium hydroxide (NaOH; 96% purity), ethylene glycol (EG), diethylene glycol (DEG), triethylene glycol (TEG), ethylene glycol monobutyl ether (EGMBE), and diethylene glycol monoethyl ether (DEGMEE) were used without purification. A standard 0.1N HCl solution was used for the titration of NaOH in the solutions. Other extra-pure-grade reagents were used without further purification.

Alkaline Depolymerization Reaction

PTT chips (3.1 g, 15 mmol on the basis of the repeating unit of monomers), NaOH (1.4 g, 35



Scheme 1 Alkaline hydrolysis of PTT.

mmol), and reaction media (40 mL) were placed in a four-necked flask reactor equipped with a reflux condenser, stirrer, and thermocouple. Under a nitrogen atmosphere, PTT was hydrolyzed while stirring for a specified period at a certain temperature in this solid/liquid reaction system. After a specified time of treatment, the reaction mixture was cooled quickly by immersing the flask in ice water and quenched by pouring into 200 mL of distilled water.

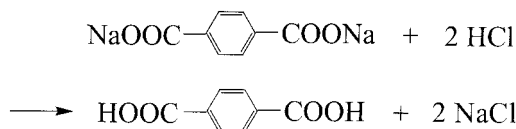
Characterization

The unreacted NaOH was titrated with a standard 0.1N HCl solution up to pH 7 to measure the amount of NaOH consumed, which was equivalent to the molar amount of sodium carboxylate formed. In a preliminary experiment, the titration values for the filtrates, which were obtained after removing both precipitated disodium terephthalate (DST) and unreacted chips, were found to be the same as those for unfiltered mixtures. Thereafter, all titrations were carried out with unfiltered mixtures. After titration, the mixture was filtered to remove undecomposed PTT solids, and weight loss was determined. The filtrate was acidified with concentrated hydrochloric acid to produce TPA. Both TPA and the remaining chips were dried to measure their weights. The surface morphology of PTT chips was examined with a scanning electron microscope (Hitachi S4200, Hitachi, Japan) with a magnification of 30,000 \times .

RESULTS AND DISCUSSION

Weight Decrease of PTT Chips and Yields of TPA

The final products of the alkali depolymerization are EG and DST, which precipitate quantitatively in the reaction solution (Scheme 1). The rate of weight decrease in chips is equal to the formation rate of DST. This reaction mixture was acidified



Scheme 2 TPA regeneration: acidolysis of DST.

with the excess HCl to separate TPA from the aqueous solution (Scheme 2).

The weight change of PTT chips during the reaction is shown in Figure 1. Hydroxide ions attack the molecular chain simultaneously, causing the short chain to be stripped into the liquid phase; weight loss thus results. The depolymerization rate was accelerated by increasing the temperature. At 190°C, complete depolymerization was attained in about 60 min. The yields of isolated TPA corresponded exactly to the decrease in the molar amount of the PTT chips.

Kinetics of Alkaline Depolymerization

The rate of alkaline depolymerization, being equivalent to the rate of DST formation, can be expressed with eq. (1) on the basis of Scheme 1:²²

$$d[-\text{COONa}]/dt = k'[-\text{ROOC}(\text{C}_6\text{H}_4)-][\text{NaOH}] - k''[-\text{COONa}][\text{HO}(\text{CH}_2)_3\text{OH}] \quad (1)$$

Based on the assumption that the reaction proceeds on the chips surface, $[-\text{ROOC}(\text{C}_6\text{H}_4)-]$ is the concentration of ester function on the surface, which can be considered roughly constant for a certain period of time. The concentration of DST can be considered as zero because it is insoluble and precipitates. The amount of NaOH consumed is equivalent to a double mole of DST; therefore, eq. (1) is transformed to eq. (2), as follows:

$$d[-\text{COONa}]/dt = k[\text{NaOH}] = k(C_0 - [-\text{COONa}]) \quad (2)$$

where $k = k'[-\text{ROOC}(\text{C}_6\text{H}_4)-]$ and C_0 is the initial concentration of NaOH. The integration of this equation leads to eq. (3), as follows:

$$\ln(C_0/(C_0 - [-\text{COONa}])) = kt \quad (3)$$

Figure 2 represents the plot of formation of DST as a function of time, with an initial concentration of PTT (1 mol/L) and NaOH (2 mol/L). Kinetic data from Figures 2 and 3 were introduced into eq. (3) to calculate the rate constant.

In view of the experimental results, the reaction seemed to be composed of two stages, a slow initial stage (rate constant k_1) and a fast second stage (rate constant k_2). PTT had superior resistance to alkaline depolymerization and heat sta-

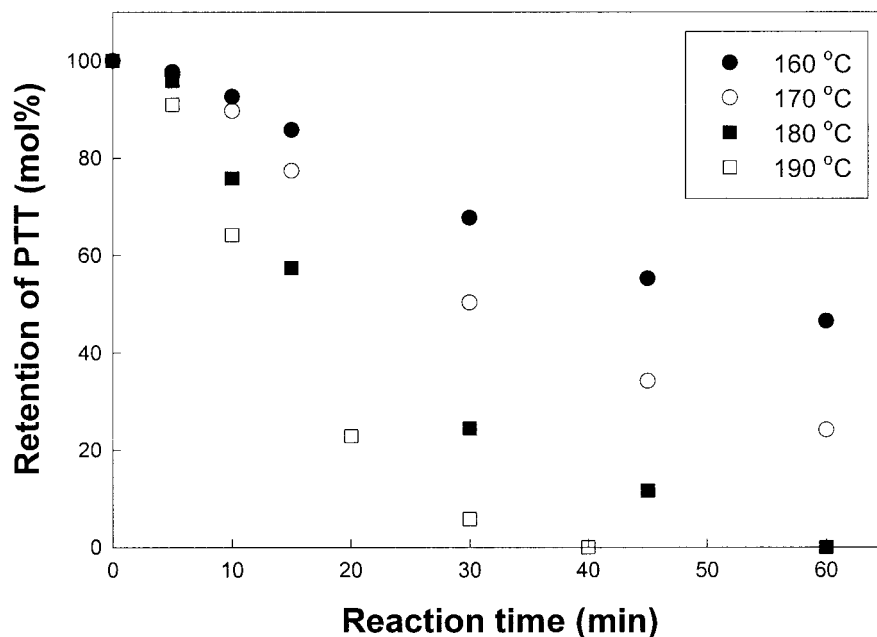


Figure 1 Plot of PTT weight loss versus reaction time.

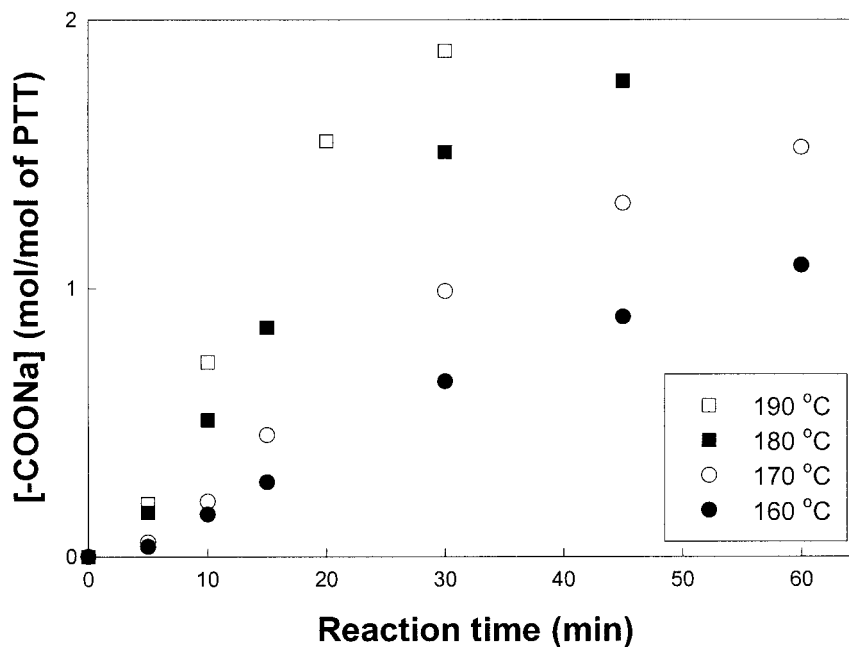


Figure 2 Plot of $[-\text{COONa}]$ versus reaction time.

bility, which may have been due to a twisted chain conformation. Mark²³ used rotational isomeric state theory to calculate the values of the conformational partition function (Z) and entropy (S) for polyoxide chains with repeating units $[(\text{CH}_2)_y-\text{O}-]$. Z had a maximum value that corresponded to maximum equilibrium flexibility of

the chain at $y = 3$, whereas the characteristic ratio $\langle r^2 \rangle_0/nl^2$ (unperturbed dimensions relative to the number of skeletal bonds and the average square of their length) was at the minimum. This also suggests that amorphous PTT chains may have a crumpled conformation. The crumpled conformation of the glycol residue may interfere

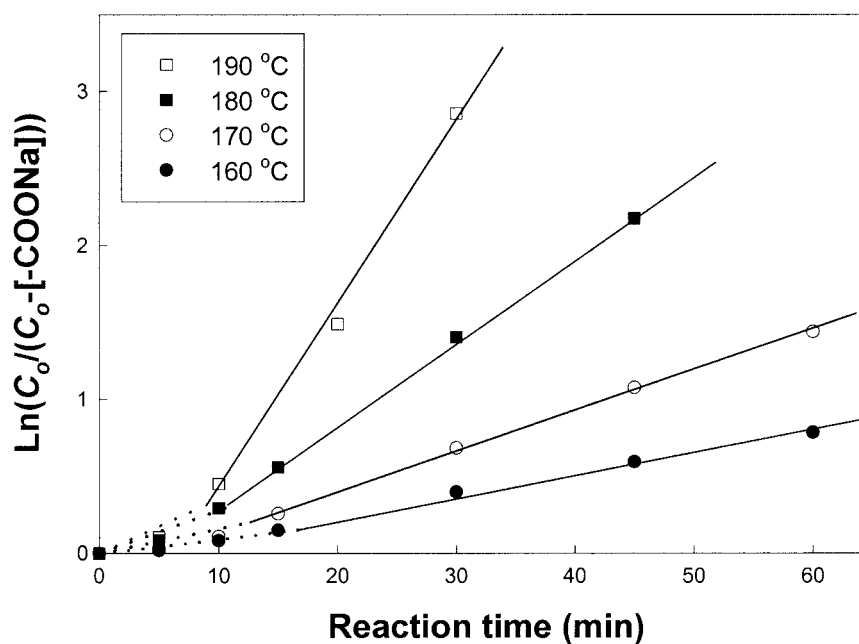


Figure 3 Plot of $\ln[C_o/(C_o - [-\text{COONa}])]$ versus reaction time.

Table I Reaction Rate Constants for the Alkaline Depolymerization of PTT in Ethylene Glycol

Reaction Temperature (°C)	k_1 (min ⁻¹)	k_2 (min ⁻¹)
160	0.0085	0.0140
170	0.0108	0.0262
180	0.0294	0.0541
190	0.0450	0.1203

with the diffusion of hydroxide ions. Accordingly, we regarded the initial stage as an induction period. As the reaction temperature was increased, the induction period was gradually shortened. The rate constants k_1 and k_2 , shown in Table I, were calculated from the data in Figure 3.

Effect of Adding Ethers

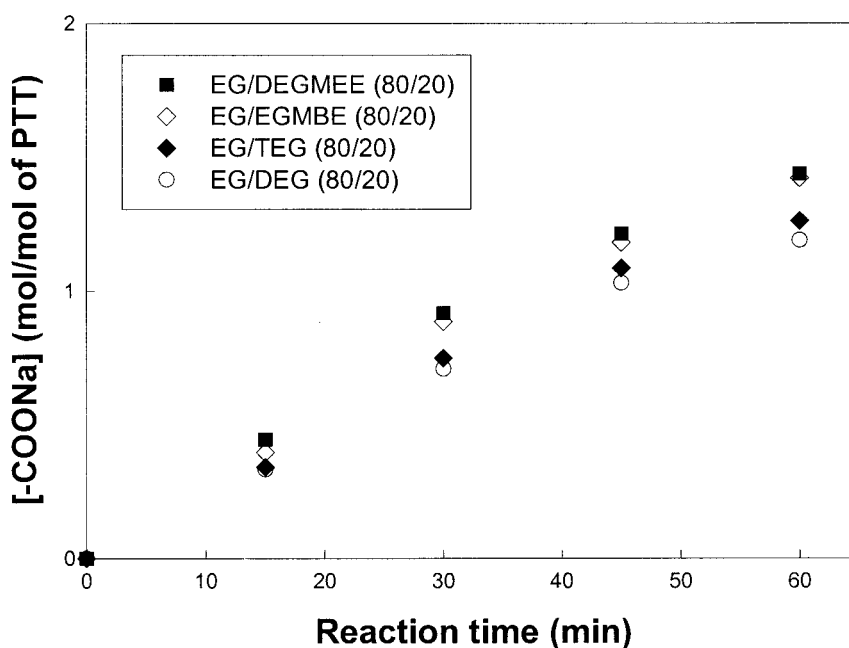
The addition of ethereal solvents, such as DEG, TEG, EGMBE, and DEGMEE, to EG slightly accelerated the rate of the alkaline depolymerization of PTT (Fig. 4). We expected ethereal solvents to open the structure of solid PTT, accelerate the diffusion of hydroxide ions, and increase the ion strength of hydroxide ions.²⁴ Contrary to our expectations, mixing ethereal solvents with a ratio up to 20 vol % did not affect the acceleration of the

depolymerization reaction much. Thus, we sought the proper mixing ratio of ethereal solvents in EG. The results are shown in Figure 5. In all cases, the rate of depolymerization increased by order of 1 with an increase in the ethereal solvents and in the order DEG < EGMBE < DEGMEE. The rate constants in Table II, depicted in Figure 6 for the reaction in ethereal solvents (100%), show that the second stage was 2–14 times faster than in EG.

Relation Between Solubility Parameters and Reaction Rate

Solubility parameters are extensively applied and highly valued by the polymer chemist confronted with specific practical problems. Introduced by Hildebrand, the total solubility parameter (δ) is given by the square root of the cohesive energy density and, thus, is taken as a measure of the energy required to disrupt the intermolecular forces that hold molecules in the condensed state.²⁶ The solubility of a given polymer in various solvents is largely determined by its chemical structure. As a general rule, structural similarity favors solubility. These facts described previously indicated that the solubility of a given polymer in a given solvent is favored if the solubility parameters of polymer and solvent are equal.

The thermodynamic criteria of solubility are based on the free energy of mixing (ΔG_M):

**Figure 4** Effect of added ethereal solvent on the formation of —COONa at 160°C.

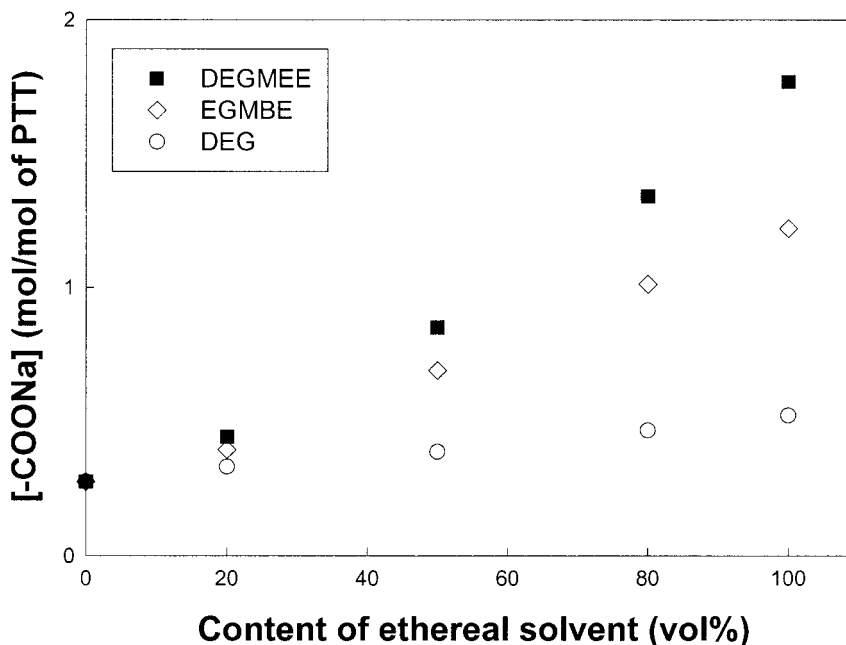


Figure 5 Effect of mixed medium on the formation of —COONa at 160°C.

$$\Delta G_M = \Delta H_M - T\Delta S_M \quad (4)$$

where ΔH_M and ΔS_M are the enthalpy and entropy of mixing, respectively. Because ΔS_M is generally positive, there is a certain limiting positive value of ΔH_M below which dissolution is possible. According to Hildebrand, the enthalpy of mixing can be calculated from

$$\Delta H_{MV} = \phi_1\phi_2(\delta_1 - \delta_2)^2 \quad (5)$$

where ΔH_{MV} is the enthalpy of mixing per unit volume; ϕ_1 and ϕ_2 are the volume fractions of components 1 and 2; and δ_1 and δ_2 are the solubility parameters of components 1 and 2, respectively. If $\delta_1 = \delta_2$, $\Delta H_{MV} = 0$ from eq. (5). So, two substances with equal solubility parameters should be mutually soluble because of the nega-

tive entropy factor.²⁷ This is in accordance with the general rule that chemical and structural similarity favor solubility.

In contrast to low-molecular-weight compounds, where solubility parameters can be directly calculated from heat of vaporization measurements, the solubility parameters of polymer specimens must be determined indirectly by swelling measurements of a slightly crosslinked polymer in a series of solvents of known solubility parameters or by calculation from molar attraction constants. A common method used to estimate polymer solubility parameters involves calculation with group molar attraction constants.²⁸ At first glance, it appears a trivial task to calculate the solubility parameter of a polymer. One only has to consider the groups present in the repeating unit of the polymer; refer to tables of molar attraction constants (F) attributed to either Small,²⁹ Hoy,³⁰ or van Krevelen,²⁷ and use the relationship:

$$\delta = \sum F_i/V \quad (6)$$

where F_i is the molar attractive constant of the atomic and structural groups forming the residue and V is the molar volume of the residue. Table III shows the results of such a calculation for PTT (δ_{PTT}) compared with the solubility parameters of

Table II Alkaline Depolymerization Reaction Rate Constants for PTT in Various Solvents

Reaction Medium	k_1 (min ⁻¹)	k_2 (min ⁻¹)
EG	0.0102	0.0140
DEG	0.0195	0.0271
TEG	0.0326	0.0407
EGMBE	0.0482	0.0908
DEGMEE	0.0524	0.1927

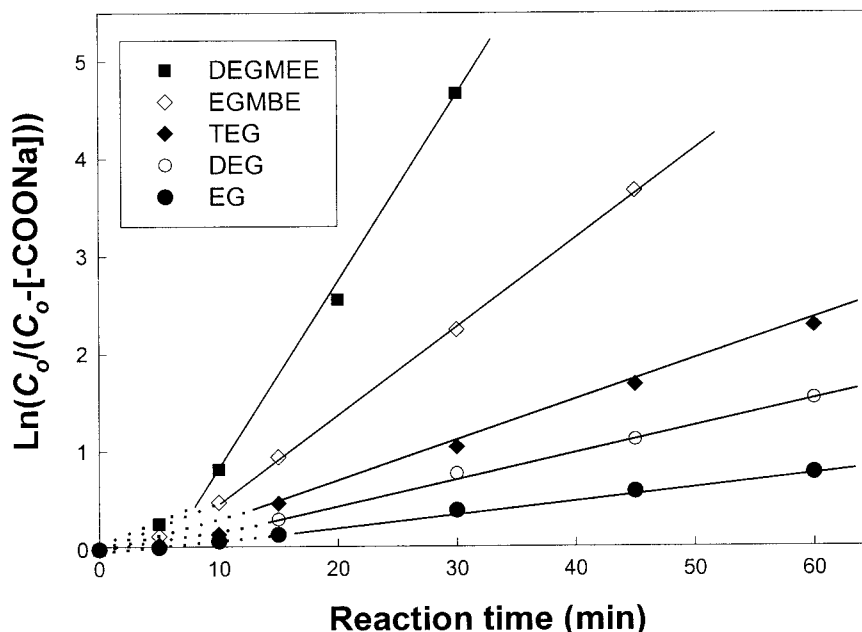


Figure 6 Plot of $\ln[C_o/(C_o - [-COONa])]$ versus reaction time for the alkaline depolymerization of PTT in ethereal medium at 160°C.

reaction solvents (δ_s). As the difference between δ_{PTT} and δ_s decreased in the order $EG > DEG > TEG > EGMBE > DEGMEE$, the reaction rate increased.

Morphological Changes by Alkaline Depolymerization

The smooth surface of a PTT chip not treated with alkali solution became markedly pitted as alkali treatment proceeded (Fig. 7). Generally, the depolymerization rate of esters is proportional to

the product of the ester. In this system, the ester concentration was equivalent to the surface area of the PTT chip. Consequently, the acceleration of degradation could be brought about because of an increase in the specific surface area of PTT by the formation and growth of pits.

CONCLUSIONS

By investigating the alkaline depolymerization behavior of PTT in EG and various ethereal solvents, we were able to draw the following conclusions:

1. A higher reaction temperature and longer reaction time yielded a faster depolymerization rate.
2. The depolymerization reaction appeared composed of two stages. The first stage was an induction period. In the second stage, the weight loss of the chips increased linearly with length of exposure to sodium hydroxide.
3. The rate of depolymerization increased by an order of 1 as the amounts of ethereal solvents increased and in the order $DEG < EGMBE < DEGMEE$. The reaction rate increased with an increase in the mixing ratio of ethereal solvents.

Table III Calculated Solubility Parameters of the Reaction Solvents and PTT³¹

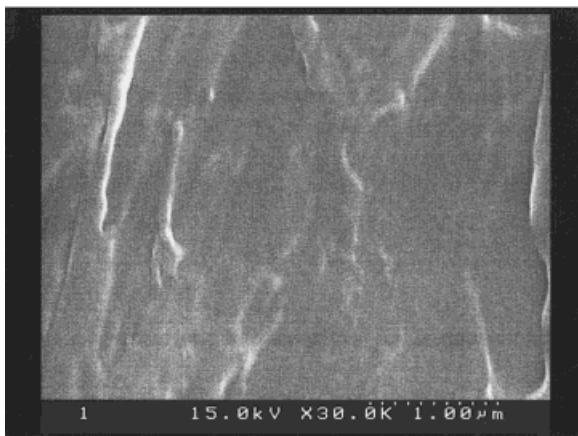
Solvent	Solubility Parameter [(cal/cc) ^{1/2}]			
	δ_d^a	δ_p^b	δ_h^c	δ_t^d
EG	8.31	5.38	12.71	16.08
DEG	7.92	7.18	10.02	14.60
TEG	7.82	6.11	9.09	13.44
EGMBE	7.82	2.49	6.01	10.17
DEGMEE	7.92	4.50	9.01	10.90
PTT				11.37

^a Dispersion component of solubility parameter.

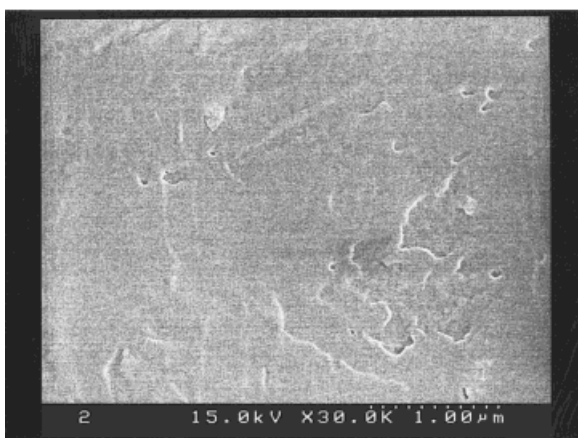
^b Polar component of solubility parameter.

^c Hydrogen bonding component of solubility parameter.

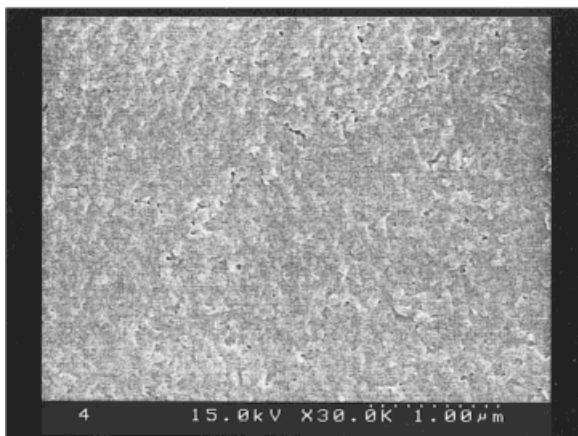
^d Total solubility parameter.



(a)



(b)



(c)

Figure 7 Scanning electron micrographs of PTT chips: (a) untreated, (b) treated for 15 min at 160°C with NaOH/EG solution, and (c) treated for 60 min at 160°C with NaOH/EG solution.

- As the difference of solubility parameters between PTT and reaction solvents decreased in the order EG > DEG > TEG > EGMEE > DEGMEE, the reaction rate increased.

In the near future, we will investigate the purity of TPA obtained from the alkaline depolymerization of PTT and the possibilities of generating raw materials. Also, we will report on the alkaline depolymerization of PTT fibrous materials such as fiber and film.

This research was supported by the Yeungnam University grants in 2000 and by the RRC research fund. The authors thank Dr. Tonelli and Miss Magdalena Kotek for useful suggestions.

REFERENCES

- Oppermann, W.; Traub, H. L.; Hirt, P.; Herlinger, H. Presented at the International Man-Made Fibers Congress, Austria, 1995.
- Brown, H. S.; Chuah, H. H. Presented at the International Man-Made Fibers Congress, Dornbirn, Austria, 1996.
- Brown, H. S.; Chuah, H. H. *Chem Fibers Int* 1997, 47, 72.
- Kim, A. S.; Kim, G. J. *J Korean Fiber Soc* 1990, 27, 23.
- Ji, B. C.; Yoon, W. S.; Kim, S. Y. *J Korean Fiber Soc* 1993, 30, 379.
- Yoon, W. S.; Lee, S. H.; Son, T. W.; Ji, B. C.; Choi, K. S. *J Korean Fiber Soc* 1996, 33, 282.
- Park, J. B.; Cho, H. H.; Kikutani, T. *J Korean Fiber Soc* 1998, 35, 125.
- Poulin-Dandurand, S.; Pérez, S.; Revol, J.-F.; Brisse, F. *Polymer* 1979, 20, 419.
- Desborough, I. J.; Hall, I. H.; Neisser, J. Z. *Polymer* 1979, 20, 545.
- Kim, Y. H.; Kim, K. J.; Lee, K. M. *J Korean Fiber Soc* 1997, 34, 860.
- Kim, Y. H.; Lee, H. M.; Kim, J. C. *J Korean Fiber Soc* 2000, 37, 118.
- Ward, I. M.; Wilding, M. A. *J Polym Sci Polym Phys Ed* 1976, 14, 263.
- Traub, H. L.; Hirt, P.; Herlinger, H. *Chem Fibers Int* 1995, 45, 110.
- Ponnusamy, E.; Balakrishnan, T. *Polym J* 1985, 17, 473.
- Mencik, Z. *J Polym Sci Polym Phys Ed* 1975, 13, 2178.
- Jakeways, R.; Ward, I. M.; Wilding, M. A.; Hall, I. H.; Desborough, I. J.; Pass, M. G. *J Polym Sci Polym Phys Ed* 1975, 13, 799.
- Campanelli, J. R.; Kanal, M. R.; Gooper, D. G. *J Appl Polym Sci* 1993, 48, 443.

18. Paszun, D.; Spychaj, T. *Ind Eng Chem Res* 1997, 36, 1373.
19. Masuda, T.; Miwa, Y.; Hashimoto, K.; Ikeda, Y. *Polym Degrad Stab* 1998, 61, 217.
20. Kook, Y. H.; Choi, C. N. *J Korean Fiber Soc* 1984, 21, 13.
21. Yoshioka, T.; Sato, T.; Okuwaki, A. *J Appl Polym Sci* 1994, 52, 1353.
22. Oku, A.; Hu, L.-C.; Yamada, E. *J Appl Polym Sci* 1997, 63, 595.
23. Mark, J. E. *J Chem Phys* 1977, 67, 3300.
24. Hu, L.-C.; Oku, A.; Yamada, E.; Tomari, K. *Polym J* 1997, 29, 708.
25. Samders, M.; Zeronian, S. H. *J Appl Polym Sci* 1982, 27, 4477.
26. Knox, B. H. *J Appl Polym Sci* 1997, 21, 225.
27. van Krevelen, D. W. *Properties of Polymers*; Elsevier Science: Amsterdam, 1990; pp 189–225.
28. Coleman, M. M.; Serman, C. J.; Bhagwagar, D. E.; Painter, P. C. *Polymer* 1990, 31, 1187.
29. Small, P. A. *J Appl Chem* 1953, 3, 71.
30. Hoy, K. J. *J Paint Technol* 1970, 42, 76.
31. Barton, A. F. M. *Handbook of Solubility Parameters and Other Cohesion Parameters*; CRC: Florida, 1985; pp 153–158.