Alkali Decomposition of Poly(ethylene terephthalate) with Sodium Hydroxide in Nonaqueous Ethylene Glycol: A Study on Recycling of Terephthalic Acid and Ethylene Glycol

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ABSTRACT: Pellets of poly(ethylene terephthalate) (PET; 0.48–1.92 g) were heated in anhydrous ethylene glycol (EG; 5 mL) with 2-equivs of NaOH at 150°C for 80 min or 180°C for 15 min to convert them quantitatively to disodium terephthalate (Na$_2$-TPA) and EG. The disodium salt was precipitated quantitatively in pure state from the EG solution and separated readily. The other product EG, being the same component to the solvent, remains in the solution and can be obtained after distillation as a part of the solvent. The rate of decomposition was significantly accelerated by the addition of ethereal solvents to EG, such as dioxane, tetrahydrofuran, and dimethoxyethane. The reaction system is simple; no water and no extra reagent other than NaOH and EG are used. A few recycling systems of PET can be designed on the basis of the present alkali decomposition reaction. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **63:** 595–601, 1997

Key words: poly(ethylene terephthalate) (PET); chemical recycling of PET; recycling of terephthalic acid; ethylene glycol; alkali decomposition of PET

INTRODUCTION

Fundamental innovations must be achieved by the human society in its life-style and philosophy in hope of establishing its sustainable development, which harmonizes with the global ecological system. Doubtlessly, the recycling of plastics is one of the major current problems we must solve due to the foreseen shortage in petroleum resources and to waste problems. Therefore, our efforts must be centered on the recycling of these precious organic resources derived from petroleum.

In the last decade, efforts were devoted mainly to the physical transformation of plastic wastes into other plastic forms[1,2] due mainly to economical reasons. However, in this style of recycling, the reutilization market is limited because (1) the turnover of the recycling is at most two, and (2) pure plastic materials, equivalent to the original one, are not available due to contamination. Therefore, in parallel to this style of recycling, other styles of reutilization in the form of monomers have been extensively studied.

We focused our attention on the recycling of poly(ethylene terephthalate) (PET) in the form of their monomers terephthalic acid and the diols. In literature, a number of hydrolysis and alcoholysis studies of PET have been reported. For example, PET can be hydrolyzed in aqueous phase by acids[3,4] and strong bases.[5] However, the following are problems. (1) PET is not soluble in aqueous solutions, (2) ethylene glycol (EG), which is one of the products, cannot be separated easily from the aqueous solution; hence, the wastewater treatment becomes a problem. To solve the first problem, hydrolysis under supercritical conditions of water has been studied with efficient results.[6–8] However, we are skeptical of such a study, which requires such specific conditions as
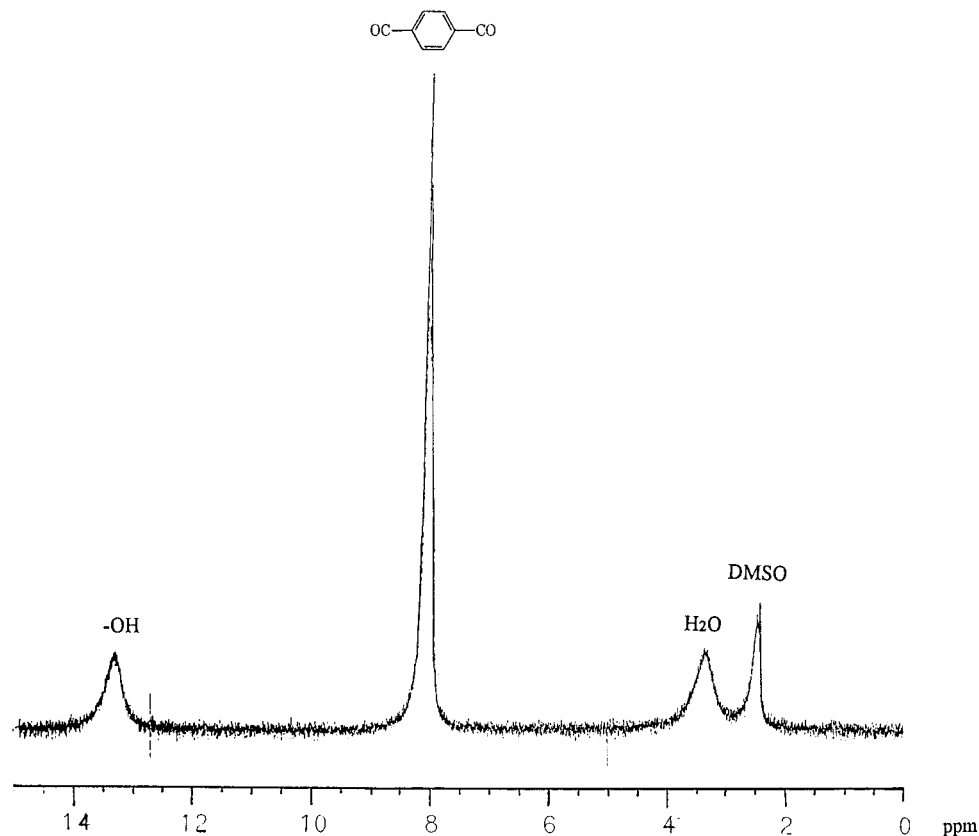
Figure 1 ^{1}H-NMR spectrum of TPA obtained from the alkali-decomposition of PET heated at 160°C for 25 min and precipitated by the addition of hydrochloric acid.

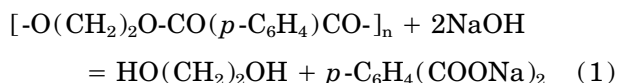high pressures, high temperatures, and special apparatuses.

Alcoholysis also seems successful. Methanolysis[9] and ethylene glycolysis[10–15] are of particular interest because they can afford dimethyl terephthalate and di(hydroxyethyl) terephthalate, respectively, which can also be used as the starting monomers of polymerization. Some problems in alcoholysis are (1) the use of catalysts, (2) severe treatment conditions, (3) inefficacy of alcoholysis producing some amount of oligomers, and (4) isolation of the products from EG.

Based on the above-mentioned literature survey, we summarized that the encountered problems fit into four overall categories:

1. surface reactivity of solid PET, which composes the major rate-determining stage;
2. high temperatures and pressures, which determine the safety and cost of the process;
3. product separation and their purity;
4. simplicity of the process and the use of inexpensive reagents.

These problems seem to have been solved in our present simple study (eq. 1).* EG is used as the solvent, sodium hydroxide is the only one reagent, and reaction conditions are mild (150–180°C for 60–15 min) under the atmospheric pressure. Products are EG and disodium terephthalate (Na$_2$-TPA), which precipitates quantitatively in the EG solution. The surface reactivity of PET in EG increases at 150–180°C, and the rate of weight decrease in pellets is equal to the formation rate of Na$_2$-TPA so that no PET oligomers cannot be formed in the solution.

$$[\text{-O}(\text{CH}_2)_2\text{O-CO}(p\text{-C}_6\text{H}_4)\text{CO-}]_n + 2\text{NaOH}$$

$$= \text{HO}(\text{CH}_2)_2\text{OH} + p\text{-C}_6\text{H}_4(\text{COONa})_2 \quad (1)$$

EXPERIMENTAL

Reagents and PET Samples

Pure PET pellets (2 mm length $\times$ 1 mm diameter, MW = 30,000) were used as the standard sub-

*A similar alkali-decomposition has been appeared recently in which mixed solvents of an alcohol and an aprotic polar solvent, such as N-methylpyrrolidone or dimethyl sulfoxide, are used. Neither the single use of EG nor the combined use of EG with an ether was mentioned [JP 502964 (1996), WO 94/10121].

strate instead of PET wastes. Commercially available NaOH (96% purity) and ethylene glycol (EG) were used without purification. For the titration of NaOH in the solutions, a standard $1N$-HCl solution was diluted to $0.2N$ with distilled water and used.

## Sample Reaction Procedure and Rate Measurement

PET pellets (0.48–1.92 g), NaOH (0.21–0.84 g), and EG (5 mL) were placed in a test tube under a nitrogen atmosphere, and the mixture was warmed to 150–180°C under stirring. After a specified time of treatment, the reaction tube was cooled quickly in a cold water, and the mixture was poured into 50 mL of distilled water and titrated with standard $0.2N$ HCl solution up to pH 7 to measure the amount of NaOH consumed (which is equivalent to the molar amount of sodium carboxylate formed). In preliminary experiments, the titration values for the filtrates, which were obtained after removing both precipitated Na_2-TPA and unreacted pellets, were found to be the same to those for unfiltered gross mixtures. Therefore, all the titrations were carried out with the gross mixture.

After titration, unreacted pellets, if remained, were removed, and the aqueous filtrate solution was acidified with concentrated hydrochloric acid to obtain terephthalic acid (TPA). Both TPA and the remained pellets were dried to measure their weights. Also, ^1H NMR of TPA and X-ray fluorescence (XRF) spectra of the remained pellets, and Na_2-TPA were measured.

RESULTS AND DISCUSSION

^1H NMR Analysis

A white powder of Na_2-TPA, which was formed during the course of reaction in EG, was separated, dissolved in water, and acidified with an excess amount of hydrochloric acid to obtain TPA. The TPA separated was dissolved in dimethyl sulfoxide-d_6, and its purity examined by the FT-^1H NMR analysis to detect the EG residue if remained in the form of oligomers or hydroxyethyl terephthalates. However, the nuclear magnetic resonance (NMR) analysis did not detect such EG residues within the detection limit (1%; see Fig. 1).
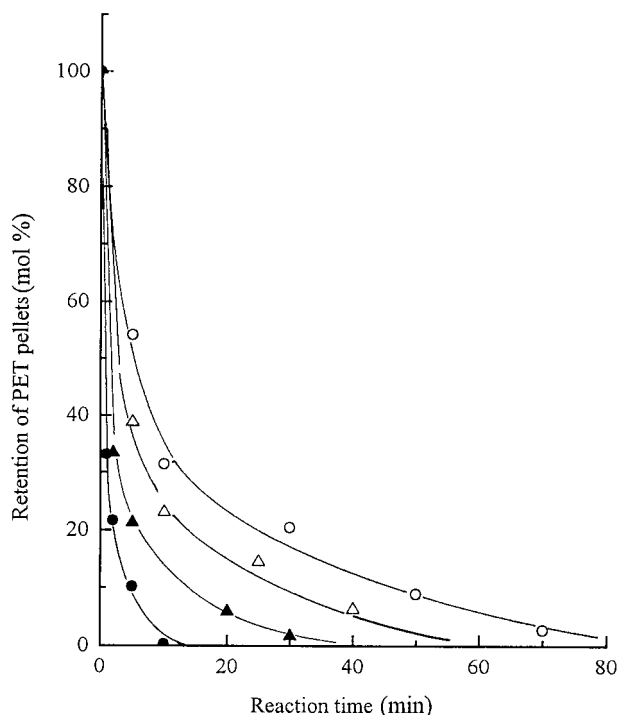
Figure 2 Decrease in the weight of PET pellets versus reaction time at 150 (○), 160 (△), 170 (▲), and 180°C (●).

Weight Decrease in PET Pellets

A change in the weight of the pellets during the course of the reaction is shown in Figure 2. The decomposition rate is accelerated by raising the temperature; and the time required for a complete decomposition is 80, 50, 30, and 15 min at 150, 160, 170, and 180°C, respectively.

Yields of TPA

The yields of isolated TPA are shown in Figure 3. The reaction at 180°C for 15 min yielded TPA quantitatively, and any reaction in which the pellets are completely dissolved can attain almost quantitative formation of TPA.

Alkali Decomposition Process on the Surface of the Pellets

Figures 2 and 3 show that the yields of TPA correspond exactly to the decrease in the molar amount of the pellets. This indicates that the alkali decomposition takes place on the surface of the pellets, but not in solution, and any intercept of the reaction during the course does not affect the amount and purity of Na_2-TPA formed by that moment. XRF analysis on isolated Na_2-TPA and
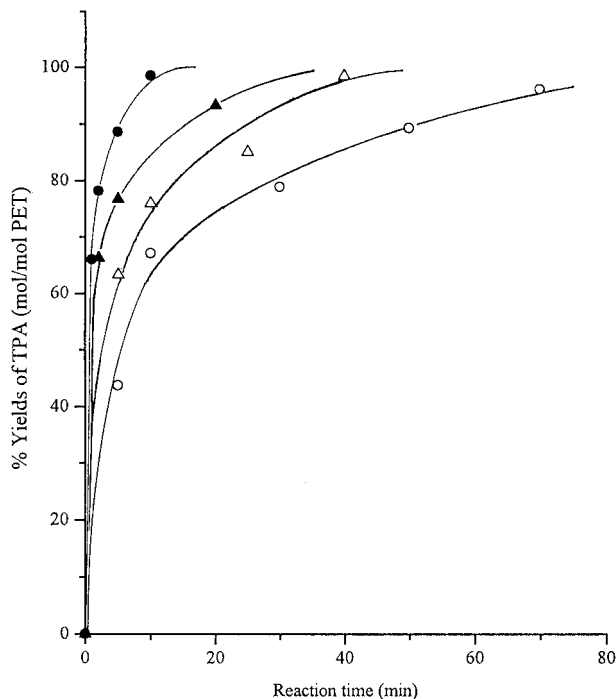
Figure 3 Effect of temperature on the yield of TPA versus reaction time at 150 (○), 160 (△), 170 (▲), and 180°C (●).

the remaining pellets are shown in Figure 4. The white powder of Na_2-TPA shows a strong diffraction peak of sodium at 55.19 (deg) (2θ), whereas the remained pellets shows no diffraction. This also indicates that the alkali decomposition takes place on the pellet surface but leaves no sodium salt there.

Kinetic Measurements

First of all, the effect of heating a NaOH/EG solution on the titration values, but in the absence of PET, was examined to assure the titration background of kinetic measurements. A 5 mL of EG, in the presence of NaOH (0.21–0.84 g) but in the absence of PET, was heated at 180°C for 30–60 min. Titration of a diluted reaction mixture revealed that such heating for a certain period of time did not affect the titration values, as shown in Table I.

Figure 5 shows the kinetic of the formation of Na_2-TPA in the reaction with initial concentrations of PET (1 mol/L) and NaOH (2 mol/L), which corresponds exactly to that of Figure 3.

The rate of alkali decomposition, being equivalent to the rate of Na_2-TPA formation, can be expressed with eq. (2) on the basis of eq. (1), as follows:

$$d[\text{-COONa}]/dt = k_1[\text{-ROCOAr-}][\text{NaOH}]$$
$$-k_2[\text{-COONa}][\text{EG}] \quad (2)$$
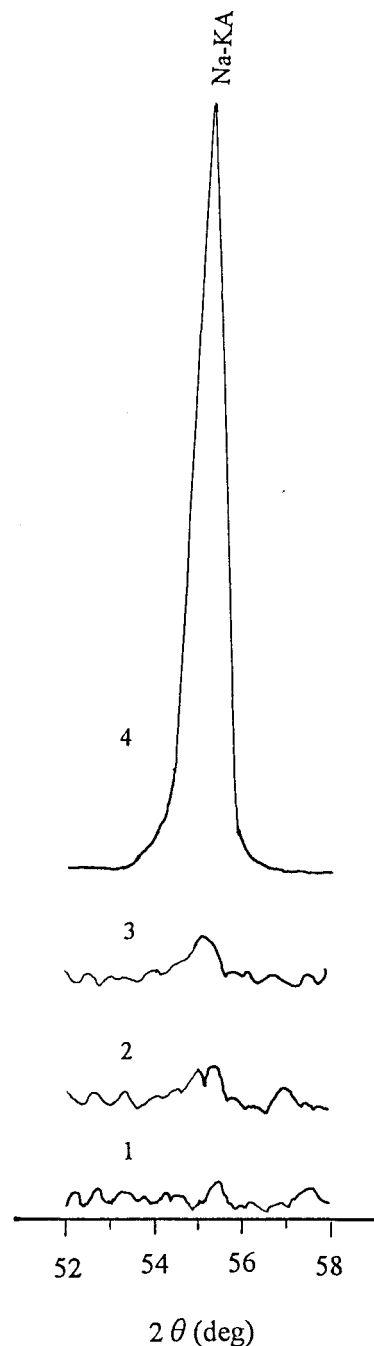
Figure 4 XRF spectra of (1) untreated PET; recovered PET pellets after alkali-decomposition (2) at 150°C for 30 min; (3) at 160°C for 25 min; and (4) disodium terephthalate obtained after these treatments.

On the assumption that the reaction proceeds on the pellet surface, [-ROCOAr-] is the concentration of ester function on the surface, which can be considered roughly constant for a certain period of time. The concentration of [Na_2-TPA] can be considered zero because it is insoluble and precipi-

Table I Titration of NaOH Heated in Ethylene Glycol at 180°C for 30 and 60 min

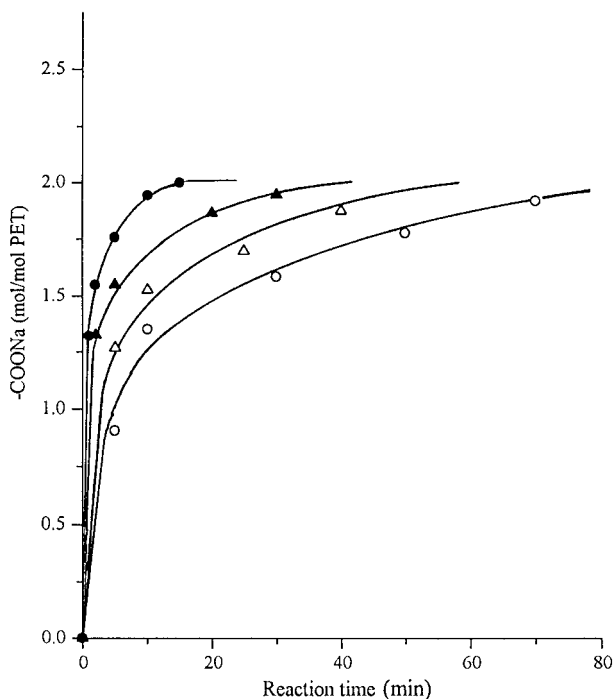| Heating Time (min)	Concentration of NaOH (g/5 mL)	HCl (mmol/g NaOH)[a]
0	0.4013	24.29
30	0.4000	24.25
60	0.4020	24.33

[a] Commercially available guaranteed-grade NaOH was used.

tates. The amount of NaOH consumed is equivalent to two-times mole of Na_2-TPA; therefore, eq. (2) is transformed to eq. (3), as follows:

$$d[\text{-COONa}]/dt = k[\text{NaOH}]$$
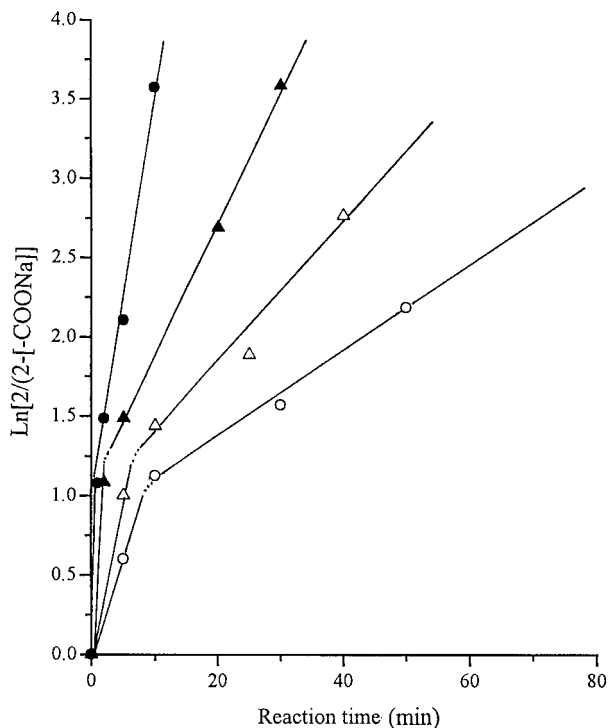$$= k[C_O\text{-}[\text{-COONa}]] \quad (3)$$

Here, $k = k_1[\text{-ROCOAr-}]$, C_O = initial concentration of NaOH. The integration of this equation leads to eq. (4), as follows:

$$\ln[C_O/[C_O\text{-}[\text{-COONa}]]] = kt \quad (4)$$

Kinetic data shown in Figure 5 are translated into

Figure 6 Transformation of Figure 5 to a kinetic expression according to eq. (4).

eq. (4) to be shown in Figure 6. Of special interest, the reaction seems to consist of two stages, i.e., a fast initial stage (rate constant k_a) and a slow second stage (k_b) following thereafter. Our explanation is this: in the first stage, the surface of the pellets can contact readily with dissolved NaOH in EG; but in the second stage, the surface is constantly covered by a certain small amount of Na_2-TPA solid, although it is constantly precipitated from the pellets. Based on this assumption, rate constants k_a and k_b are calculated from the data shown in Figure 6 as well as in Table II. In addition, Arrhenius plotting of the constants, shown in Figure 7, produced two parallel linear relationships. This indicates that the activation energies of the two stages are the same, while frequency factors are different. This unique relation may be

Figure 5 Formation of -COONa (determined by titration) versus reaction time at 150 (○), 160 (△), 170 (▲), and 180°C (●).

Table II Reaction Rate Constants for the Alkali Decomposition of PET in Ethylene Glycol

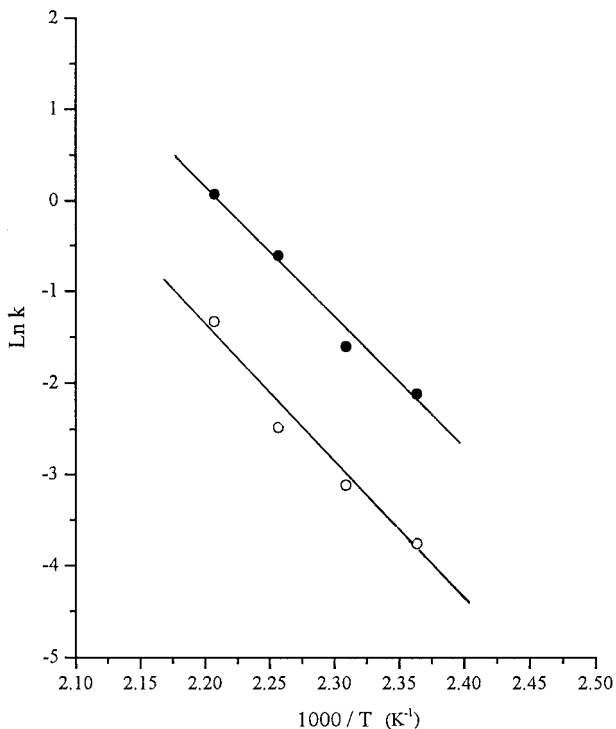| Temperature (°C)	k_a (min^{-1})	k_b (min^{-1})
150	0.1206	0.0234
160	0.2005	0.0443
170	0.5418	0.0836
180	1.0772	0.2644

due to the difference in the surface conditions between the two stages.
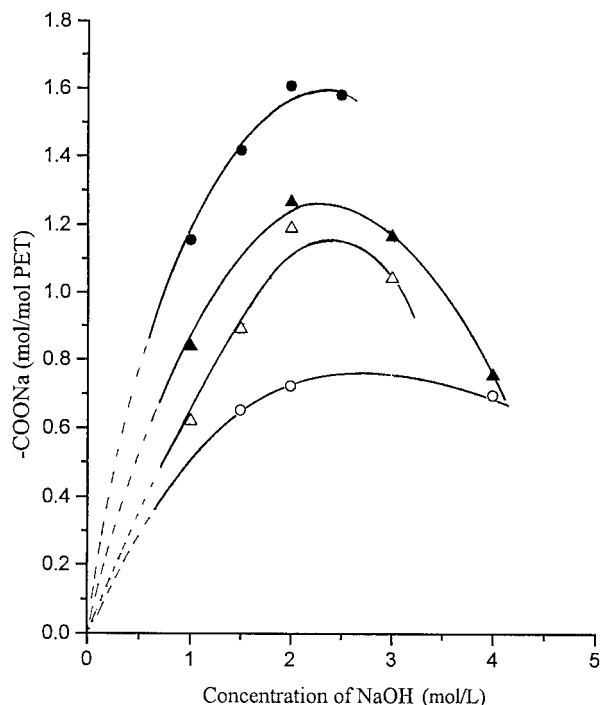
Initial Concentrations of NaOH and PET

With different initial concentrations of NaOH (1, 2, 3, and 4 mol/L), different amounts of PET (0.5, 1.0, 1.5, and 2.0 mol/L) were treated for 5 min at 160°C, and the amount of Na$_2$-TPA produced was measured to determine the effects of the initial concentrations on the reaction rates (Fig. 8). It is indicated that while the rates are accelerated by the increase in the initial concentrations of NaOH for any initial concentration of PET, the increasing tendency is retarded beyond the concentration of NaOH = 2.0 mol/L. This may be attributable to the increase in viscosity of the solution; thus, the removal of Na$_2$-TPA from the pellet surface may be slowed down.

Effects of the Addition of Ethers

The addition of ethereal solvents, such as dioxane, tetrahydrofuran (THF), and dimethoxyethane (DME), accelerated the rate of the alkali-decomposition of PET in comparison with the single use of EG. As depicted in Figure 9 for the reaction in


Figure 8 Effect of NaOH concentration on alkali decomposition of PET for various initial concentrations of PET: 0.5 (●), 1 (▲), 1.5 (△), and 2 (○) mol PET in EG (1 L).

Figure 7 Arrhenius plots for the two-step alkali decomposition with initial concentrations of NaOH (2 mol/L) and PET (1 mol/L).
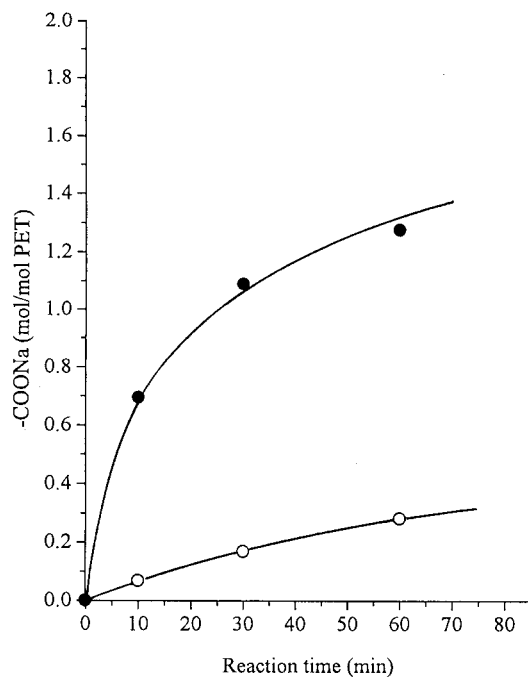
Figure 9 Effect of dioxane added to EG on the formation of -COONa in EG (○), and in a mixed solvent of dioxane with EG (20/80 vol %) (●) at 100°C.
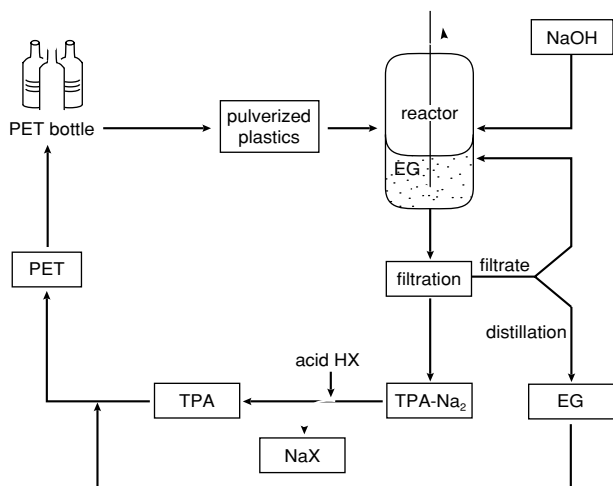
Scheme I

a mixed solvent of dioxane and EG (20/80 vol %) at 100°C, the rate was accelerated twelve times faster than in EG only. The same trend was also observed in other mixed solvents of EG with THF or DME. Again, in these solvents, the kinetic data showed that the reaction seems to proceed via two stages, as already explained for Figure 5. Therefore, we think that the ethereal additive may activate the nucleophilic power of hydroxide ion but not alter the surface condition of the pellets toward the attack by the hydroxide ion.

CONCLUSIONS

Alkali decomposition of PET in EG was revealed to be an efficient method for the reproduction of terephthalic acid (TPA) and ethylene glycol (EG) from the recovered PET plastic wastes under mild conditions. The efficiency of monomers' reproducibility and separation is remarkably high so that the procedure seems to be usable as one of the practical methods for the recycling of PET plastics, thus contributing to the plastic waste problems. The characteristics of the present method is illustrated in Scheme 1.

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