

Glycolytic Aminolysis of Poly(ethylene terephthalate) Waste for Recovery of Value-Added Comonomer at Atmospheric Pressure

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Received 18 March 2003; accepted 13 May 2003

ABSTRACT: Reaction of poly(ethylene terephthalate) waste (PETW) powder with ethylene glycol (EG) using 0.003 mol lead acetate as a catalyst was carried out in a batch reactor at 470 K under atmospheric pressure. Reactions were undertaken with various particle sizes ranging from 50 to 512.5 μm and reaction times ranging from 10 to 60 min at 10-min intervals. A low molecular weight product of PETW was obtained using this reaction. Then hydrazine monohydrate, chlorobenzene, and cyclohexylamine (CHA) were introduced to convert the low molecular weight product of PETW into terephthalohydrazide (TPHD). To increase the PETW conversion rate, an external catalyst (lead acetate) was introduced during the reaction. The reaction product was deposited onto the surface of unreacted PETW that was removed from the surface by introducing dimethyl sulfox-

ide. To accelerate the reaction rate CHA was introduced during the second stage of reaction, which has industrial significance. Depolymerization of PETW was proportional to the reaction time and inversely proportional to the particle size of PETW. Analyses of value-added products (TPHD and EG) as well as PETW were undertaken. A kinetic model was developed and experimental data were simulated consistent with the model. A thermodynamic study was undertaken because this is required during the transfer of laboratory data through the pilot plant for commercialization. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 3437–3444, 2003

Key words: poly(ethylene terephthalate) waste (PETW); comonomers; catalysts; kinetics (polym.); thermodynamics

INTRODUCTION

The thermoplastic polyester group of polymers includes saturated polyesters like poly(ethylene terephthalate) (PET), a most important polyester, that is principally recognized for its use in consumer materials dating back to 1953. In the late 1970s, interest was directed toward the development of faster crystallizing grades of PET suitable for various applications. The current usage of PET has primarily been as an engineering thermoplastic along with several other polyesters. PET wastes (PETW) can be recycled. Although recycled PET cannot be used for beverage bottles, it can be used in the manufacture of other products such as insulation boards or can be thermally or chemically repolymerized to its monomers, which can then be used for the polymerization of virgin polyesters. PET waste is a polyester of terephthalic

acid (or dimethyl terephthalate) and ethylene glycol. The growing interest in PET recycling is attributed to the widespread use of film and packaging with PET. Increased quantities of PET are used for production of soft drink bottles, and a further increase in its application is predicted.

A very important feature of PET, decisive in the choice of its wide application in manufacture of packaging for the food industry, is that it does not have any known side effects on human organism. PET does not create a direct hazard to the environment, but because of its substantial fraction by volume in the waste stream and its high resistance to the atmosphere and biological agents, it is seen as a noxious material. Ecological as well as economic considerations advocate introduction of wide-scale PET recycling of traditional materials such as glass, paper, or metals. Recycling of waste PET can be carried out in many ways. A very attractive form of recycling of used polymer materials is the so-called materials recycling, which consists of collection, disintegration, and granulation of waste polymer followed by their recirculation into production. Among other methods of polymer recycling, chemical recycling—applied above all in the case of postconsumer condensation polymers—is of great interest. Availability of a wide spectrum of de-

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Contract grant sponsor: National Chemical Laboratory, Pune, M.S., India.

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polymerizing agents and a large variety of products (e.g., monomers for polymer and resin synthesis and other additives for polymeric materials) are some of the advantages of PET chemical recycling.^{1,2}

Chemical recycling processes implemented for PET nearly parallel the manufacture of PET on a commercial scale. Initially, chemical recycling found an application as a way to use wastes generated during the production cycle of PET. Historical and practical reasons cause processes of chemical depolymerization of PET to be usually divided as methanolysis, glycolysis, hydrolysis, ammonolysis, aminolysis, and other processes.^{3,4} The second most important method in chemical processing of PET is glycolysis. This process is used widely on a commercial scale. PET degradation is carried out most frequently using ethylene glycol (EG).⁵⁻¹¹ Very few investigations focused on the kinetics of glycolysis reactions,^{7,10} but their rates were very low and were not of any industrial significance. Chen et al.¹⁰ concluded that the glycolysis rate was second order with respect to EG concentration, and that EG thus acts as both reactant and catalyst in glycolysis. It contradicts the earlier findings of Challa.¹² Baliga and Wong⁷ determined that the glycolysis reaction was first order with respect to EG concentration. Yields of monomeric products were almost equal to those of PET conversion.^{3,4,13} Depolymerization of PETW was proportional to the reaction time^{3,4,13} and inversely proportional to the particle size of PETW.^{3,4,13}

In the past there were no detailed required data available about product characterization, kinetics, and thermodynamics that were necessary for process development of glycolytic aminolysis of PET. Published data depend on specific experimental procedures and resulting kinetic parameters vary with the assumed kinetic model and applied data-fitting procedure. In the absence of a reliable model and reaction data, reaction engineers have been forced to scale-up and to establish the reactors in economically undesirable small steps. Additionally, available reaction data are insufficient for designing new reactor concepts with justifiable expenditure.

This study was undertaken (1) to understand the correct reaction order and (2) to obtain high-quality terephthalohydrazide (TPHD) as a high value added comonomeric product. TPHD is used as a comonomer for preparation of a polyhydrazide comonomer and converted into the corresponding bis(azodicarbonyl) derivative, and it is extremely expensive. TPHD can also be produced from expensive fine chemicals, but costs of production are also very high. In this study TPHD was recovered during depolymerization of PETW at a comparatively low manufacturing cost, thus making the procedure of industrial significance. PETW particle size and reaction time were optimized. A kinetic model was developed and validated with our own experimental data. The glycolysis rate was

improved significantly by the addition of cyclohexamine (CHA) and dimethyl sulfoxide (DMSO) in EG that resulted in complete conversion of PETW in less time than that of commercial processes. A thermodynamic study was undertaken because this is required during the transfer of laboratory data through the pilot plant for commercialization.

EXPERIMENTAL

Materials, chemicals, and reagents

The PETW used in this study was procured from Garaware Polyesters (Aurangabad, M.S., India). Here "waste" means materials left over after some products (e.g., films) were made from raw material. The other materials used were neutral water, methanol, CaO, sodium sulfate, EG, lead acetate (LA), hydrazine monohydrate (HMH; $\text{H}_2\text{NNH}_2 \cdot \text{H}_2\text{O}$), dimethyl sulfoxide (DMSO), and cyclohexylamine (CHA), obtained from S. D. Fine Chemicals (Mumbai, India). These chemicals were used as received without further purification.

Glycolytic aminolysis of PETW

Glycolysis was undertaken in a 500-mL four-neck round-bottom flask equipped with an RTD (resistance temperature detector), a stirrer, and two reflux condensers at 470 K and at atmospheric pressure. The reaction was carried out by mixing 10 g PETW in 40 mL EG with 5 mL DMSO using 0.003 mol LA as a catalyst with four pieces of porcelain for different periods of reflux time ranging from 10 to 60 min at 10-min intervals. Different particle sizes ranging from 50 to 512.5 μm of PETW were taken for this reaction (separately). After completion of the glycolysis reaction, the batch reactor was removed from the heating mantle and unreacted PETW (if any) was separated, collected, and washed with neutral water and then with alcohol to remove deposition on the PETW surface, if any. Collected unreacted PETW was dried in a controlled oven at 353 K until achieving a constant weight.

After removing unreacted PETW, if any, the resulting liquid phase was placed in the batch reactor that was cooled to 298 K. Into this reaction mixture 6.6 mL HMH, 7 mL chlorobenzene, and 1 mL CHA were introduced. It was stirred at 298 K for 25 min to obtain a precipitate; the batch reactor was kept in an ice bath to cool to 283 K for 5 min to obtain precipitation of complete product (TPHD). The resulting precipitate of product (TPHD) was separated from rest of the materials by filtration. The TPHD product was washed with hot neutral water and then with alcohol to remove the catalyst and other impurities, if any, from

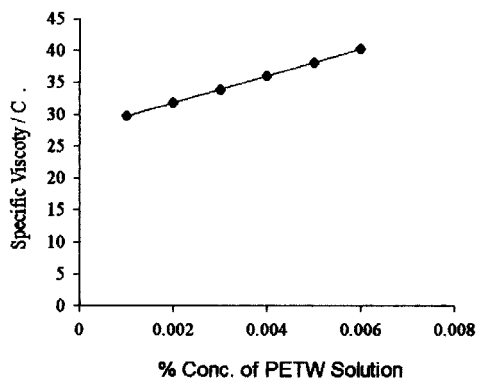


Figure 1 Effect of % concentration of PETW solution on specific viscosity.

the TPHD. Collected TPHD was dried in a controlled oven at 353 K until achieving a constant weight.

From the resulting waste liquid phase, EG was recovered using a salting-out method by introduction of sodium sulfate.

Both products (TPHD and EG) were analyzed qualitatively and quantitatively. Percentage depolymerization of PETW, yield of TPHD, and yield of EG were determined by gravimetry and defined as follows:

Depolymerization of PETW (%)

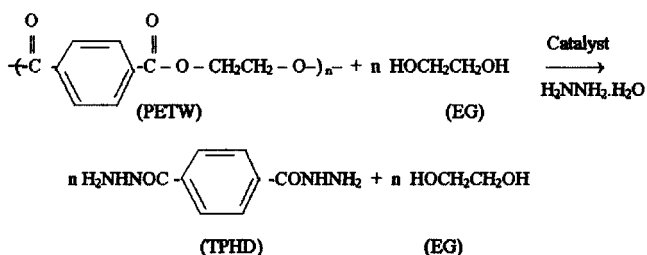
$$= \frac{W_{PETW,i} - W_{PETW,R}}{W_{PETW,i}} \times 100 \quad (1)$$

$$\text{Yield of TPHD (\%)} = \frac{m_{TPHD,O}}{m_{PETW,i}} \times 100 \quad (2)$$

$$\text{Yield of EG (\%)} = \frac{m_{EG,O}}{m_{PETW,i}} \times 100 \quad (3)$$

where $W_{PETW,i}$ is the initial weight of PETW, $W_{PETW,R}$ is the weight of unreacted PETW, $m_{TPHD,O}$ is the number of moles TPHD, $m_{EG,O}$ is the number of moles of EG, and $m_{PETW,i}$ is the initial number of moles of PET monomeric units.

Process reaction for glycolytic aminolysis of PETW



EG recovery method

EG was recovered by using a previously reported salting-out method,² based on the introduction into

the filtrate of sodium sulfate to obtain a saturated solution, resulting in the formation of a separate organic layer. Calcium oxide in quantities equivalent to the ratio of sodium sulfate and sulfuric acid content was added and simultaneously mixed into the aqueous layer obtained in the first variant. The precipitated calcium sulfate was separated by a suction filtration technique. The remaining aqueous solution of sodium hydroxide was then recycled back into the process.

Determination of molecular weight of control and residual PETW

The viscosity-average molecular weight (M_v) of control PETW at 298 K was determined by Ostwald’s viscosity method. The solvent used was a mixture of phenol and tetrachloroethane at a ratio of 3 : 5 (v/v). A clean and dry Ostwald’s viscometer was used to determine the time of flow for the solvent mixture by keeping the viscometer in a thermostat to maintain a constant temperature. Various solutions (0.001–0.006%) of PETW were prepared in the solvent mixture. The flow time of each solution was also recorded. The effect of concentration (C) of PETW on viscosity (η_{sp}) is shown in Figure 1, where the y-intercept was recorded as 27.7 mL/g. By retaining the values¹⁴ of Mark–Houwink constants ($k = 22.9 \times 10^{-3}$ mL/g, $\alpha = 0.73$) and y-intercept for the mixture, M_v was determined by the relation¹⁴ $\eta_{sp}/C = kM^\alpha$. The molecular weight determination of residual PETW was also undertaken at 433–473 K at 10-K intervals.

Qualitative analysis of products (EG and TPHD)

Liquid (EG) and solid (TPHD) products obtained from glycolytic aminolysis of PETW were analyzed by determining their various spectra (FTIR and NMR) and physical properties (e.g., melting point, boiling point, molecular weight, etc.) to confirm the products.

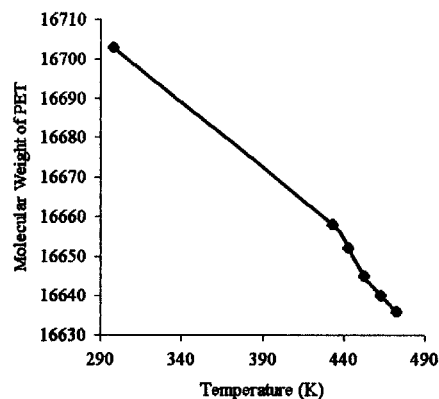


Figure 2 Variation of molecular weight of PET with temperature (K).

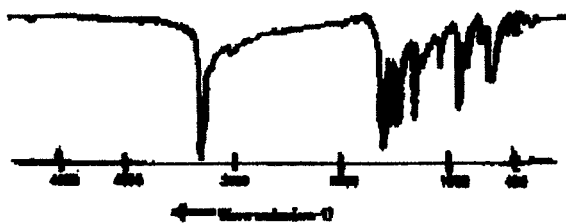


Figure 3 IR spectra (KBr) of TPHD.

RESULTS AND DISCUSSION

Determination of molecular weight of control and residual polyesters

The M_v value of PETW at 298 K was recorded as 16,703 g mol^{-1} . Molecular weight determinations of residual polyesters were also undertaken at 433–473 K at 10-K intervals (Fig. 2). The molecular weight of residual PETW was slightly decreased with an increase of reaction temperatures. However, at a higher temperature (i.e., 473 K), the molecular weight of residual PETW was 16,636, still close to 16,703 g mol^{-1} . The slight decrement in molecular weight might be attributable to the decrease in viscosity with the increase in temperature. Therefore, the bulk phase of residual PETW was close to that of fresh PETW having long chains. This suggests that depolymerization of PETW powder occurred on the external surface of the PETW powder, and PETW powder was lamellarly depolymerized.

Analysis of products (EG and TPHD)

The liquid product obtained from glycolytic aminolysis of PETW was analyzed by determining its weight per mL (1.113), boiling point (470 K), and molecular weight (62 g mol^{-1}). These results were close to the values for EG.

The solid product obtained from glycolytic aminolysis of PETW was melted at 575 K and molecular weight was 194 g mol^{-1} . These results were close to the values for TPHD.

Figure 3 shows FTIR (KBr) spectral absorption with

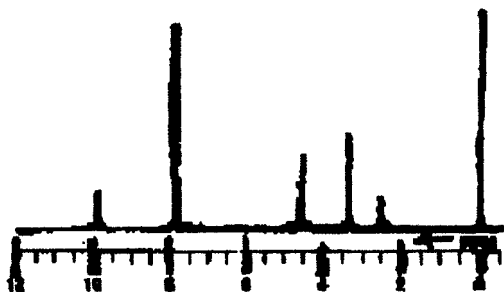


Figure 4 $^1\text{H-NMR}$ spectra ($\text{DMSO-}d_6$) of TPHD.

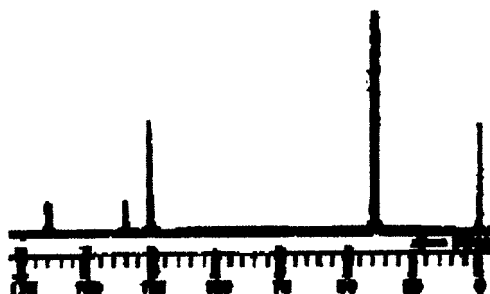


Figure 5 $^{13}\text{C-NMR}$ spectra ($\text{DMSO-}d_6$) of TPHD.

wavenumbers 1503, 1540, and 1630 cm^{-1} for the aromatic group, amide group I, and amide group II, respectively. Figure 4 shows the $^1\text{H-NMR}$ spectra with δ value 7.85 ppm for aromatic protons, δ 9.85 ppm for amide protons, and δ 4.54 ppm attributed to the presence of NH protons. Figure 5 shows $^{13}\text{C-NMR}$ spectra with δ 126.9 ppm for ArC—H, δ 135.4 ppm for ArC—CO, and δ 165.4 ppm for the CO group. Various spectra (FTIR in Fig. 3, $^1\text{H-NMR}$ in Fig. 4, and $^{13}\text{C-NMR}$ in Fig. 5) of the solid product confirm that TPHD was the solid product obtained from glycolytic aminolysis of waste PET.

Optimization of particle size of PETW for glycolytic aminolysis

Results of optimization of particle size of PETW for glycolytic aminolysis are shown in Figure 6 (for 20 min of reflux time in the presence of CHA). Particle sizes from 50 to 512.5 μm were obtained and it was observed that with greater particle size PETW conversion was decreased. Initially PETW conversion was constant and maximum (100%) for particle sizes of 50, 64, 90, and 127.5 μm . However, later PETW conversion was decreased with higher particle size (181, 256, 362.5, and 512.5 μm), which indicates that PETW con-

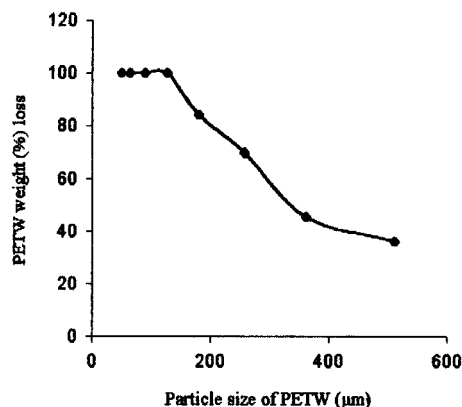


Figure 6 Optimization of particle size of PETW for glycolytic aminolysis.

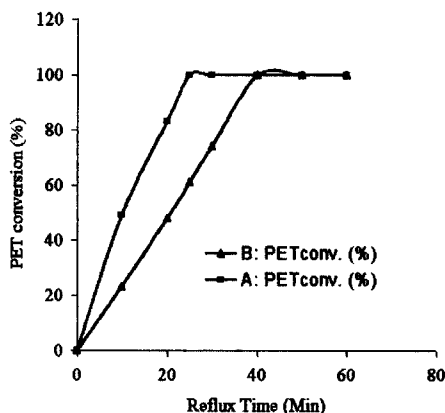


Figure 7 Optimization of reaction time for catalytic glycolytic aminolysis of PETW: (A) with cyclohexylamine; (B) without cyclohexylamine.

version was inversely proportional to the particle size of PETW. The optimal PETW size, which is the maximum particle size at which PETW conversion is maximum, was recorded as 127.5 μm (Fig. 6).

Optimization of reaction time for glycolytic aminolysis of PETW

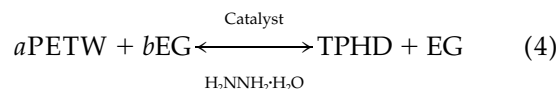
By maintaining the particle size of PETW at 127.5 μm, the reaction time was optimized, varying from 10 to 60 min for depolymerization of PETW with [Fig. 7(A)] and without [Fig. 7(B)] introduction of CHA. PETW conversion was initially less, although with further increases of time PETW conversion was found to increase up to reaction time periods of 20 min (A) and 40 min (B), respectively. After 20 min (A) and 40 min (B) of reaction time, respectively, there was no increase in PETW into products. Optimal PETW conversion (100%) was recorded at 20 min (A) and 40 min (B), respectively, for glycolytic aminolysis of PETW into optimal recovery of products (Fig. 7), which clearly indicates that PETW conversion into products was proportional to the reaction time. The optimal time is the time at which the PETW conversion is maximum, after which it remains constant.

Effect of reaction time on recovery of value-added products

Table I shows the results of effect of time on PET conversion, yield of TPHD, and yield of monomeric EG at 1 atm during depolymerization of PET. It was observed that on increasing reaction time from 10 to 40 min, PET conversion (%), yield of TPHD, and yield of monomeric EG were increased. Yields of TPHD and EG were almost equal to PET conversion (Table I); moreover, PET conversion was improved significantly by using CHA in EG (Table I).

Kinetic modeling and simulation of glycolytic aminolysis of PETW

Glycolytic aminolysis of PETW occurs at equilibrium with the reverse reaction given as



where *a* is the initial concentration of ethylene diester (EDE) groups of polymer PETW and *b* is the initial concentration of EG.

For the initial time periods of reaction the reverse reaction is not important because its rate is very low and can be omitted. Thus the rate of disappearance of polyester EDE groups is equal to the rate of formation of product TPHD that is given by the following stoichiometric equation:

$$-r_{\text{EDE}} = \frac{-dC_{\text{EDE}}}{dt} = \frac{dC_{\text{TPHD}}}{dt} = kC_{\text{EG}}C_{\text{EDE}} \quad (5)$$

$$\frac{dC_{\text{TPHD}}}{dt} = \frac{dx}{dt} = kC_{\text{EG}}C_{\text{EDE}} \quad (6)$$

where *C* is concentration, $-r_{\text{EDE}}$ is the rate of reaction of depolymerization; $-dC_{\text{EDE}}/dt$ is the rate of disappearance of EDE groups; dC_{TPHD}/dt is the rate of formation of product TPHD; *k* is the second-order rate constant of reaction; *t* is the reaction time; *x* represents

TABLE I
Effect of Time on PET Conversion, Yield of TPHD and Yield of Monomeric EG at 1 atm During Depolymerization of PET^a

Time (min)	A: PET conv. (%)	TPHD yield (%)	EG yield (%)	B: PET conv. (%)	TPHD yield (%)	EG yield (%)
10	49.1	49	48.97	23	22.98	22.96
20	83	82.97	82.95	48	47.96	47.95
25	100	99.98	99.98	61	60.98	60.98
30	100	99.98	99.98	74	73.98	73.97
40	100	99.98	99.98	100	99.98	99.98

^a A, with cyclohexylamine; B, without cyclohexylamine.

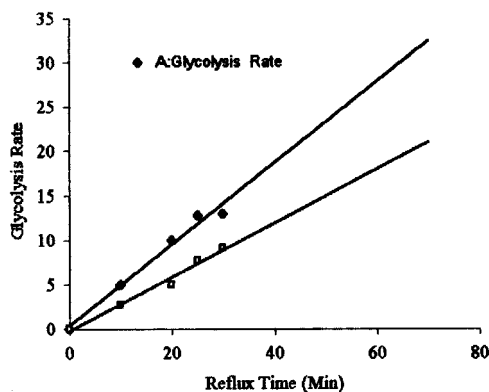


Figure 8 Effect of reaction time on catalytic glycolytic aminolysis rates with model eq. (13) at 473 K using lead acetate catalyst: (A) with cyclohexylamine; (B) without cyclohexylamine at atmospheric pressure for 127.5 μm particle size.

moles of EDE groups of PETW or EG reacted in time t and the degree of depolymerization of PETW; $(a - x)$ is the concentration of EDE groups of polymer PETW left behind at time t ; and $(a - b)$ is the concentration of EG left behind at time t .

Separating the variables in eq. (6) gives

$$\frac{dx}{(a-x)(b-x)} = k dt \quad (7)$$

Resolving into partial fractions for $b > a$ gives

$$\frac{1}{(a-x)(b-x)} = \frac{1}{b-a} \left(\frac{1}{a-x} - \frac{1}{b-x} \right) \quad (8)$$

Using this result, eq. (7) can be integrated as follows:

$$\frac{\int dx}{(a-x)(b-x)} = \frac{1}{b-a} \left(\int \frac{dx}{a-x} - \int \frac{dx}{b-x} \right) = k \int dt \quad (9)$$

Carrying out the integration gives

$$\frac{1}{b-a} \{ -\ln(a-x) - [-\ln(b-x)] \} = kt + \text{IC}$$

$$\frac{1}{b-a} \ln \left(\frac{b-x}{a-x} \right) = kt + \text{IC} \quad (10)$$

where IC is the integration constant. To determine the value of IC, consider that at $t = 0$, $x = 0$. Hence, from eq. (10),

$$\text{IC} = \frac{1}{b-a} \ln \left(\frac{b}{a} \right) \quad (11)$$

Substituting this value of IC into eq. (10) gives

$$\frac{1}{b-a} \ln \left(\frac{b-x}{a-x} \right) = kt + \left[\frac{1}{b-a} \ln \left(\frac{b}{a} \right) \right]$$

Rearranging and solving for kt gives

$$\frac{1}{b-a} \ln \left[\frac{b-x}{a-x} - \ln \left(\frac{b}{a} \right) \right] = kt$$

$$kt = \frac{1}{b-a} \ln \left[\frac{(a/b)(b-x)}{a-x} \right] \quad (12)$$

In general eq. (12) can be written as

$$\frac{1}{B} \ln \left(\frac{1}{1-x} \right) = kt \quad (13)$$

where $B = b - a$ is the difference in initial concentrations of EG and EDE groups; $[1/(1-x)] = [(a/b)(b-x)/(a-x)]$ for the initial time periods; and $(1/B)\ln[1/(1-x)]$ is the reaction rate of depolymerization.

We see that eq. (13) is the equation of a straight line that passes through the origin ($y = mx$), where $y = (1/B)\ln[1/(1-x)]$, $m = k$, and $x = t$.

Variable x takes a value of 0 at reaction time $t = 0$ and a value of 1 for complete (100%) conversion of PETW. Reaction time 0 is considered to be the time at which the desirable reaction temperature was first obtained in the reaction vessel. The reaction rate constant was obtained by plotting $(1/B)\ln[1/(1-x)]$ versus t , as shown in Figure 8. The initial rate with eq. (13) is seen to provide a good fit for our own experimental data. Thus from Figure 8 the glycolytic aminolysis rate of PETW expressed in eq. (13) was applicable and consistent with simulated data. The slope of the line in Figure 8 predicted the value of the rate constant. The rate of reaction was significantly improved by the addition of CHA with EG, resulting in the complete conversion of PETW into value-added products with less reflux time than that shown in Figure 8.

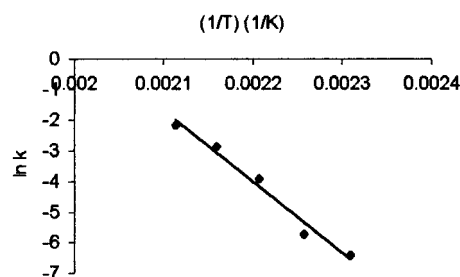


Figure 9 Arrhenius plot for catalytic glycolytic aminolysis of PETW.

TABLE II
Comparison of Activation Energy (E_a) and Arrhenius Constant (A) as Cited in Literature for Depolymerization of PETW

Parameter	Reference			
	Present work	13a	15	16
E_a (kJ/mol)	46.2	56.4	88.7	101.3
A (L/mol ⁻¹ /min ⁻¹)	99,783	—	—	—

Thermodynamic study of glycolytic aminolysis of PETW using the compensation effect

For glycolytic aminolysis of PETW, an Arrhenius plot is depicted in Figure 9. The activation energy (E_a) calculated from the slope is 46.2 kJ/mol, and the respective Arrhenius constant (A) calculated from the intercept is 99,783 L mol⁻¹ min⁻¹. The E_a value is less than the values reported by other investigators^{13,15,16} (Table II); thus glycolytic aminolysis was rate determining on the PETW surface.

Variations in these values arise from a compensation effect resulting from a change in the reaction environment (i.e., various investigators used different chemicals for depolymerization of PETW). All Arrhenius plots will pass through a common point or very close to a point. Occurrence of this common temperature at which rate constants are identical leads to calling this relationship a theta rule. It seems reasonable to consider that a large number of sites of high energy will be formed at higher temperatures during preparation of the catalyst. These sites will be most active in catalysis, given that they will have various heats of adsorption and energies of activation for surface reactions. Thus high-temperature preparations will have low energies of activation. Because there will be a few of these sites on low-temperature preparations, the energy of activation for reaction on these catalysts will be higher, although the total number of sites will be greater and so a larger number of sites will compensate for the high energy of activation. A catalyst for which energy of activation is unfavorable will have a favorable number of active sites. E_a values

increase when the rate constant decreases and vice versa (this is attributed to the change in reaction environment). It was thus concluded that compensation effects occurred during glycolytic aminolysis of PETW.

The rate constant, condensation rate constant, equilibrium constant, Gibbs free energy, enthalpy, and entropy of reaction of PETW were determined (Table III).

The data reported in Table III were obtained as follows. The values of k were determined with eq. (13). The values of K_e were calculated by replacing C_{water} with C_{EG} in eq. (9) of Campanelli et al.¹⁷ The values of k' were calculated by $k' = k/K_e$ [eq. (8) of Campanelli et al.¹⁷]. The values of Gibbs free energy (ΔG) and enthalpy (ΔH) of reaction of PET were determined by eqs. (13.11a) and (13.14), respectively, of Smith et al.¹⁸ Entropy values (ΔS) were determined by the equation (ΔS) = ($\Delta H - \Delta G$)/ T of Smith et al.¹⁸ Values of the glycolysis rate constant and equilibrium constant of reaction increase with temperature; however, values of enthalpy, Gibbs free energy, condensation rate constant, and entropy of reaction decrease with increase in temperature. This shows that the glycolysis of PET is endothermic and reversible.

Analysis of PETW sample

Analyses of PETW samples were undertaken with molecular weight of 16,703 g mol⁻¹; density, 1.41 g/cm³; melting range, 523–537 K; thermoplastic polyester; water absorption, 0.5%; and breaking strength, 50 MPa. These values were almost identical with those reported in the literature.¹⁹

CONCLUSIONS

Glycolytic aminolysis of PETW revealed that it is possible to obtain complete PETW conversion into value-added comonomeric product TPHPD and monomeric product EG. The optimal reactant size and reflux time were recorded as 127.5 μm and 20 min, respectively. Glycolytic aminolysis of PETW was proportional to the reaction time and inversely proportional to the

TABLE III
Effect of Temperature on Catalytic Glycolytic-Aminolysis Rate Constant (k), Condensation Rate Constant (k^{-1}), Equilibrium Constant (K_e), Gibbs Free Energy (ΔG), Enthalpy (ΔH), and Entropy (ΔS) for 60 min

T (K)	K_e	k ($\times 10^3$) (L/mol ⁻¹ /min ⁻¹)	k^{-1} ($\times 10^3$) (L/mol ⁻¹ /min ⁻¹)	ΔG (kJ/kmol)	ΔH (kJ/kmol)	ΔS (kJ/kmol)
433	81.91	2.653	2.05	-15,860	-115,487	-230
443	166.3	3.252	1.961	-18,834	-359,605	-669
453	1435.3	19.913	1.387	-27,377	-364,105	-777
463	9751	56.621	0.581	-35,357	-423,036	-837
473	99,562	114.32	0.114	-45,258	-471,840	-913

^a For PETW particle size of 127.5 μm , using 0.003 mol lead acetate as an catalyst.

particle size of PETW. Results suggest that EG does not have a significant role as an internal catalyst in glycolytic aminolysis of PETW. A kinetic model developed and simulated was consistent with our own experimental data. The reaction rate was significantly improved by the addition of CHA in EG, resulting in complete conversion of PETW into value-added products with less reaction time. The kinetic model for the glycolytic aminolysis of PETW was found to be close to first order in both EG and EDE concentrations.

NOMENCLATURE

A	Arrhenius constant
B	$[EG]_i - [EDE]_i$, a constant, the change in the initial concentrations of EG and ethylene diester groups
C	concentration
CHA	cyclohexylamine
DMSO	dimethyl sulfoxide
E_a	activation energy
[EDE]	concentration of ethylene diester groups
EG	ethylene glycol
[EG]	concentration of liquid EG
HMH	hydrazine monohydrate ($H_2NNH_2 \cdot H_2O$)
k	glycolysis rate constant
k'	condensation rate constant
K_e	equilibrium rate constant
LA	lead acetate
$m_{TPHD,O}$	number of moles of TPHD
$m_{PET,i}$	initial number of moles of the PET monomer unit
$m_{EG,O}$	number of moles of EG
PET	poly(ethylene terephthalate)
PETW	PET waste
TPHD	terephthalohydrazide
$W_{PET,i}$	initial weight of PET
$W_{PET,R}$	weight of unreacted PET
x	degree of depolymerization of PET
ΔG	Gibbs free energy of reaction
ΔH	enthalpy of reaction
ΔS	entropy of reaction

The authors gratefully acknowledge the technical support given by Dr. Swaminathan Sivaram, Director of National Chemical Laboratory, Pune, M.S., India. A.S.G. gratefully acknowledges the financial support given by Chairman Dadasaheb (Shri. A. N. Kadam) of Jawaharlal Nehru Engineering College, N-6, Cidco, New Aurangabad, M.S., India. The authors are also grateful for both the technological and the economic support for the literature survey given by Prof. Pratap Borade, Principal of Jawaharlal Nehru Engineering College.

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