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# Hydrothermal Depolymerization of Polyesters and Polycarbonate in the Presence of Ammonia and Amines

Toshitaka Funazukuri

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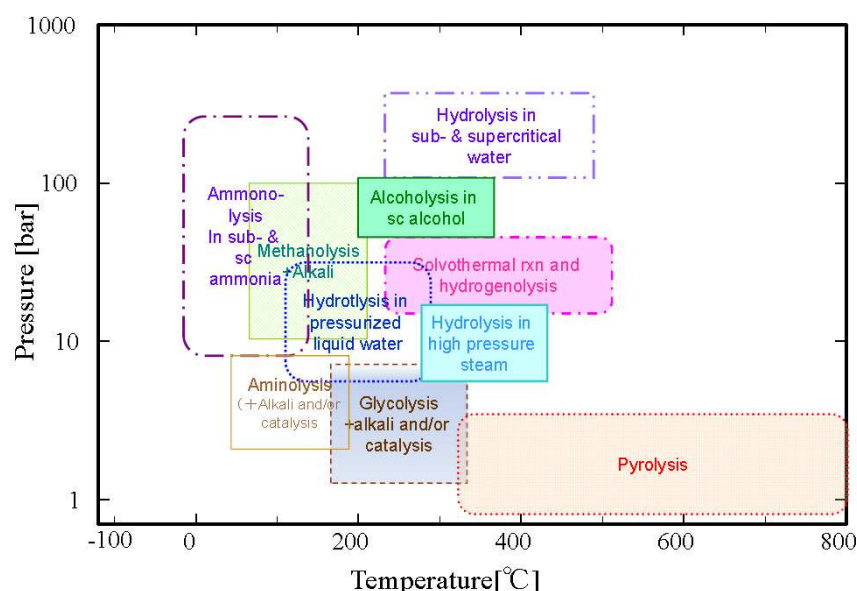
<http://dx.doi.org/10.5772/59198>

## 1. Introduction

Polyesters are widely employed as industrial uses and various consumer goods such as beverage and food bottle, container, packaging, textile etc. Along with the huge amounts of the production, the wastes are increasingly discharged around the world. Thus, the chemical recycling is essential for energy savings and developing the sustainable society.

Reaction conditions, temperature and pressure ranges, for various chemical recycling processes of polyesters are sketched in Figure 1. So far, various recycling processes for polyesters have been investigated and developed, as reviewed by Paszun and Spychaj [1]: alcoholysis with methanol or ethanol, glycolysis with ethylene glycol or propylene glycol, alkali hydrolysis with sodium hydroxide, ammonolysis and aminolysis. Recently, hydrolysis with sub- and supercritical water or with high pressure steam is also investigated. Many studies have discussed the advantages or disadvantages, and new or modified methods have been continuously developed.

The above processes have advantages, but involve some disadvantages such as severe reaction conditions of high temperature and/or pressure, the use of uncommon compounds as reaction reagents or additives, difficulty or complex procedures for the separation/purification of solvent or products, and/or low yields of the desired monomers due to undesired by-products. Moreover, even though higher monomer yields are obtained from polymer made of chiral monomer, higher reaction temperatures are unfavorable due to racemization. For instance, in conversion of poly(L-lactic acid) to lactic acid under hydrothermal conditions D-lactic acid as well as L-form was produced [2]. The yield ratio of D-form to L-form increased with increasing temperature and time, and the rate was expressed by the zeroth order reaction kinetics, namely, only as a function of temperature. To eliminate/reduce racemization of monomers produced lower reaction temperatures are preferable.



**Figure 1.** Reaction conditions for various degradation processes of polyesters.

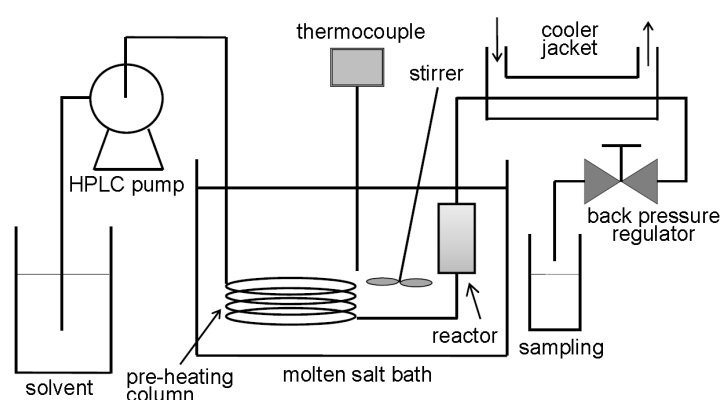
Among the various chemical recycling methods, ammonolysis and aminolysis are promising for degrading polyesters due to the high reactivities of nucleophilic reagents such as ammonia and amines toward polyesters. In conventional ammonolysis/aminolysis processes, the main objective is not to recover the monomers but to obtain amide compounds from PET for use as coating materials, plasticizers, and ingredients which have a wide range of molecular weight. However, these methods have not yet been employed in industrial processes [1], and studies have been made since the 1960s [3-7]. In fact, most initial aminolysis studies were to investigate the surface morphology or modification and the strength of PET fibers [3-7], and not to recover the monomers. No reports on the measurements of reaction rates and the yields were available. In fact, ammonolysis/aminolysis processes had not been considered to be promising for converting the polymers to monomers.

As compared with the initial studies on ammonolysis/aminolysis, the use of sub- and supercritical ammonia (critical temperature of 405.6 K and critical pressure of 11.3 MPa) is more practical. Mormmans et al. [8] reported the ammonolysis of various polymers including PET with sub- and supercritical ammonia containing water, which mainly converted the PET into terephthalamide and EG. The reaction temperature is much lower than those in other processes (see in Fig. 1).

Recently, we have carried out the depolymerization of PET in a dilute aqueous ammonia solution under hydrothermal conditions [9-12]. This process can be conducted under milder reaction conditions of temperature and dilute alkaline, which lead to preventing the reactor from corrosion. Moreover, the products are mainly the monomers, and the production of oligomers is less likely in aqueous solutions. It can be speculated that oligomers produced are not dissolved from the solid surface due to the low solubilities, and the oligomers remained in polymer and/or on the surface are further degraded to monomers. The reaction is dominated

by nucleophilic reaction with ammonia rather than alkali hydrolysis. Thus, a high concentration of ammonia/amine is not required, and ammonia/amine can be recovered by hydrolytic decomposition of the intermediate to monomers and ammonia/amine under hydrothermal conditions, whereas the intermediate products formed from some amines and polymers are stable. The products were mainly TPA and EG for PET [9-13], naphthalene dicarboxylic acid (NDC) and EG for PEN [12,14], bisphenol A for PC [12,15]. In this chapter, based on our recent studies [9-15] the effectiveness of monomerization with ammonia and amines is demonstrated in hydrothermal depolymerization of polyesters and polycarbonate.

## 2. Experimental apparatus and procedures [11-15]



**Figure 2.** Schematic diagram of a semi-batch flow reactor.

A schematic diagram of the experimental set-up is shown in Figure 2. A small semi-batch flow reactor was mainly employed, and sometimes a small bomb type batch reactor was also used. The both reactors were the same structure and size (c.a. 3.6 mL), and were made from 1/2 inch O.D. stainless-steel. First, a couple of or a few pieces of particles (ca 60 to 150 mg) were charged in the reactor, and a frit disk was placed at the exit of the reactor not to remove the polymer samples out of the reactor. Distilled water was filled in the reactor and throughout a line at room temperature. The preheating column of 1/8 inch O.D. tubing was placed in a molten salt bath, maintained at the intended value with a temperature fluctuation less than  $\pm 2$  K. At time zero the solvent was fed, and then shortly the reactor was immersed in the bath. Apart from the reaction procedure, the temperature of the solvent in the reactor was found to reach the intended value within one minute by monitoring the temperature inside the reactor with a thermocouple directly placed in the center of the reactor. The solvent was supplied in most runs at a flow rate of 3 ml/min at ambient temperature and 5.0 or 10 MPa. Note that the saturation pressures of pure water at 493 and 523 K are 2.32 and 3.98 MPa, respectively. By tracer response measurements in the previous studies we confirmed that the flow in the reactor was almost a plug flow at the flow rates higher than 2 to 3 mL/min. The residence time of the solution in the reactor was negligible so that it took less than 30 seconds for the solvent to flow

from the reactor exit to the outlet of the back pressure regulator [11-15]. The solvents eluted from the reactor were cooled down in a heat exchanger made of two co-axis cylinder tubes, 40 cm long by flowing with water. At every certain period, 2 minutes for early reaction times and 5 to 10 minutes for longer reaction times, the product solutions were collected from the outlet of the back pressure regulator. The yields of monomers in the each fraction were analyzed by HPLC. After the completion of reaction residual solid did not remain in most runs.

Due to low concentrations of ammonia and amines in the aqueous solutions, the densities of the aqueous solutions were assumed to be equal to those of pure water [16] at reaction conditions. The total organic carbon (TOC) and product yields were based on carbon weight as defined by Eqs (1) and (2), and the conversion  $y$  by Eq. (3):

$$\text{TOC}(\%) = 100 \times \frac{\text{organic carbon solution (g)}}{\text{carbon in initial polymer sample (g)}} \quad (1)$$

$$\text{Yield}(\%) = 100 \times \frac{\text{carbon in compound (g)}}{\text{carbon in initial polymer sample (g)}} \quad (2)$$

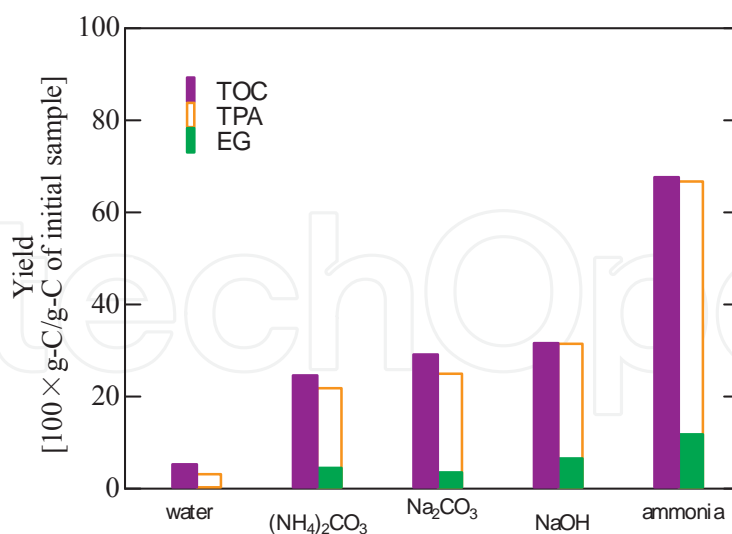
$$\text{Conversion } y(-) = \frac{\text{yield of monomer(s)}(\%)}{\text{theoretical yield of monomer(s)}(\%)} \quad (3)$$

### 3. Results and discussion

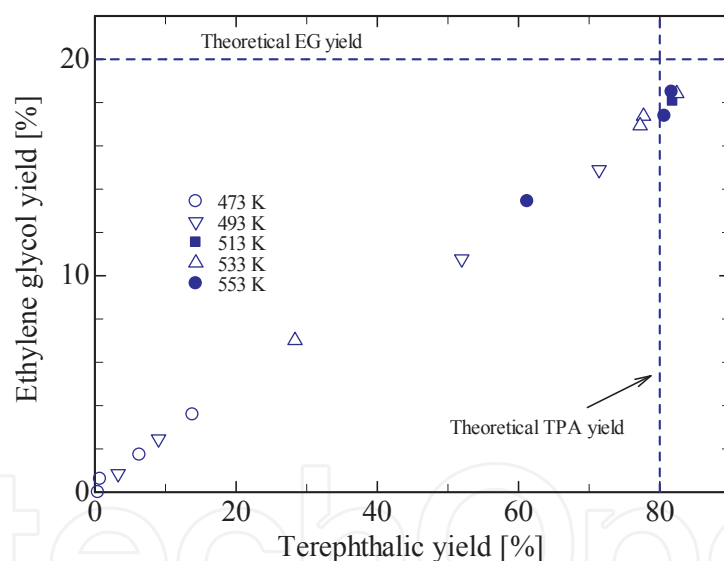
#### 3.1. PET

Figure 3 compares the effect of additives on the yields of TOC, TPA and EG at 493 K for 30 min and concentration of additives of 0.6 mol/kg in aqueous solutions except for water in a batch reactor. Ammonia was found to be the most effective, as compared to NaOH,  $\text{Na}_2\text{CO}_3$  and  $(\text{NH}_4)_2\text{CO}_3$ . The yields did not increase in the order of basicity. When no additives were present, the yields were low. The TOC yield and total yield of TPA and EG were nearly equal in all cases. Thus, TPA and EG were highly selectively produced, and yields of oligomers and by products were quite low. As described later, in comparison with amine species for PET degradation the reactivity was also not the order of amine basicity.

Figure 4 plots EG yield vs. TPA yield at temperatures from 473 K to 553 K for 5 to 30 min with a 0.6 mol/kg aqueous ammonia solution in a batch reactor. Due to the batch reactor without a stirrer, the time changes in yields were not smooth (not shown in figure), but the cross yield plots were well represented by a straight line. The yields of TPA were proportional to those of EG over an entire range of the conversion. While the yields of EG are reported to be lower than those of TPA at harsh reaction conditions, e.g. high temperature or in the presence of



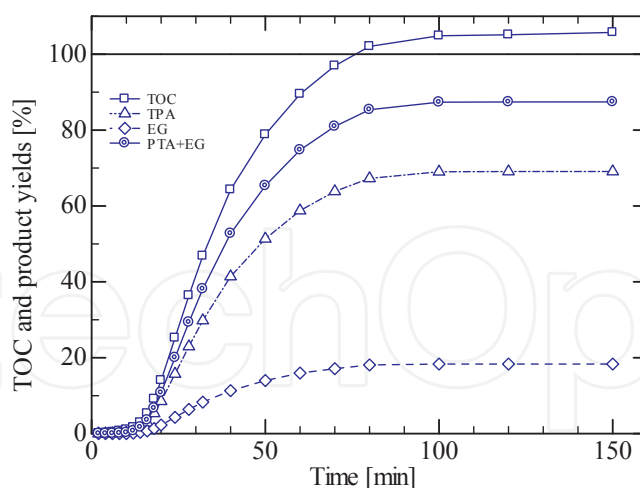
**Figure 3.** Effects of additives on TOC, TPA and EG yields at 493 K for 20 min and additive concentration of 0.6 mol/kg in a batch reactor.



**Figure 4.** EG yield vs. TPA yield at various temperatures and reaction times from 5 to 30 min with 0.6 mol/kg aqueous ammonia solution in a batch reactor [11]

strong acid, the process provides the equi-molar production of TPA and EG until the reaction is almost completed.

Figure 5 plots TOC values and product yields over flow time in an aqueous ammonia solution of 0.6 mol/kg at 483 K and a constant flow rate of 3 mL/min (at room temperature) in a semi-batch flow reactor. When the reaction was also completed after 100 min, TPA yield reached ca 70% on carbon weight basis, correspondingly 88 % of the theoretical yield, and EG did 19 % (95 % of the theoretical value). Note that from the material balances about 10 % of initial PET



**Figure 5.** TOC and product yields over flow time at 483 K and 0.6 mol/kg ammonia concentration at a flow rate of 3 mL/min (set at room temperature) in a semi-batch reactor [11].

samples were not identified in the run. Whereas TOC value (105 %) was higher than 100 %, this may result from experimental error. It is interesting that the induction period of 20 min was observed, where no elution of TOC was made, as well as TPA and EG. Since the temperature of fluid in the reactor reached the prescribed temperature within 1 min, it was the time for which ammonia solution diffused in solid sample, or decomposed products diffused out of inside solid sample. The induction time was shorter at higher temperature and/or higher concentration of ammonia. As described later, the induction times were also observed for all polymers and amines tested.

The depolymerization reaction is assumed to take place on the surface of polymer pellets in water with/without ammonia/amine and NaOH, as seen for PET, PEN and PC in aqueous solutions of ammonia, amines and sodium hydroxide [9-15] and poly(lactic acid) in water and an aqueous sodium hydroxide solution [2]. This assumption can be verified from the direct observation of PET and PC samples in a view cell in the course of reaction [9]. The sizes of the cylindrical PET and PC sample decreased with time, but the shape remained. Moreover, since the solubilities of polymers PET, PEN, PC and their degradation products are low in aqueous solutions of ammonia and amine, and the reaction temperatures are lower than the melting points of the polymers, the reaction can be considered to proceed on the surface of polymers.

Although the further studies are required to explore the reaction mechanism, the reaction can be assumed to take place on the pellet surface. Thus, the overall reaction rate is expressed by the following surface reaction model for spherical particles, as derived in Appendix:

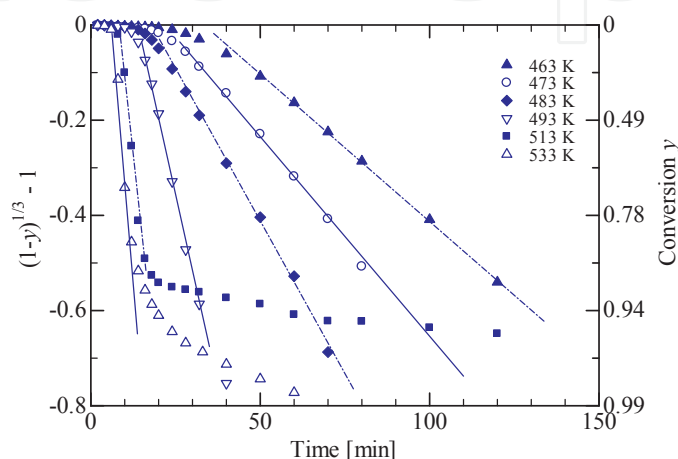
$$\frac{dy}{dt} = k(1-y)^{2/3} \quad (4)$$

$$y = 0 \quad \text{at} \quad t = t_i \quad (5)$$



where  $y$  (-) is the conversion based on the monomer yield (e.g. TPA+EG yield for PET),  $t$  and  $t_i$  are the reaction and induction times, respectively, and  $k$  (1/min) is the overall rate constant. By integrating Eq.(4) under condition of Eq.(5),

$$(1-y)^{1/3} - 1 = -\frac{k}{3}(t-t_i) \quad (6)$$



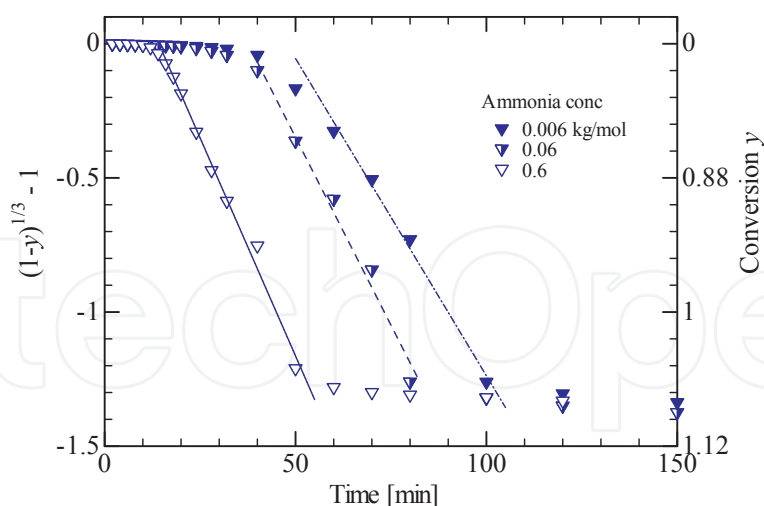
**Figure 6.** The validity of the surface reaction model in plot of  $[(1-y)^{1/3}-1]$  vs. time at various temperatures at 0.6 mol/kg ammonia concentration in a semi-batch reactor[11]. The vertical axis on the right hand side was the conversion  $y$ , corresponding to that on the left hand side  $[(1-y)^{1/3}-1]$ .

Figure 6 indicates that Eq.(6) well represents the yield data over a wide range of conversion  $y$  ( $[1-y] = 0.86$  to  $0.13$ , correspondingly  $[(1-y)^{1/3}-1] = -0.05$  to  $-0.5$ ). Note that the induction times were observed and they increased with decreasing temperatures. Since the reaction temperatures were lower than the melting point of PET, during the reaction the polymer sample was solid and was remained in the shape until the reaction was nearly completed by observing from view cell experiments.

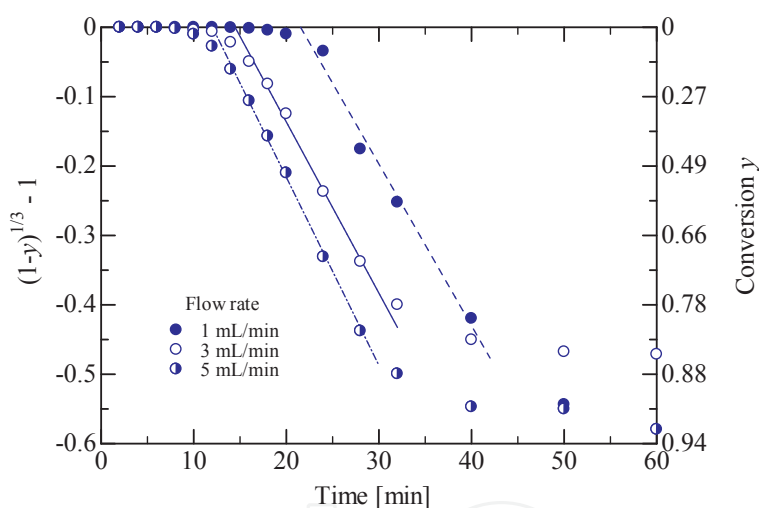
Figure 7 shows the effect of ammonia concentration on the rate [11]. Equation (6) satisfied the data, and the rate constants were  $7.11 \times 10^{-2}$ ,  $8.40 \times 10^{-2}$ ,  $9.90 \times 10^{-2}$  1/min at 0.006, 0.06 and 0.6 mol/kg, respectively. Although the rate data at the three concentrations are only available, the rate constants slightly increased with increasing ammonia concentration, but the induction time significantly decreased with increasing the concentration.

Figure 8 shows the effect of flow rate on the reaction rates in plots of  $[(1-y)^{1/3}-1]$  vs. time at 493 K and 0.6 mol/kg ammonia concentration in a semi-batch reactor. It is interesting that the flow rate significantly affected the induction time, but hardly did the slope, namely the rate. This may suggest that the dissolution of decomposed components from pellet surface to the solvent could be controlled.



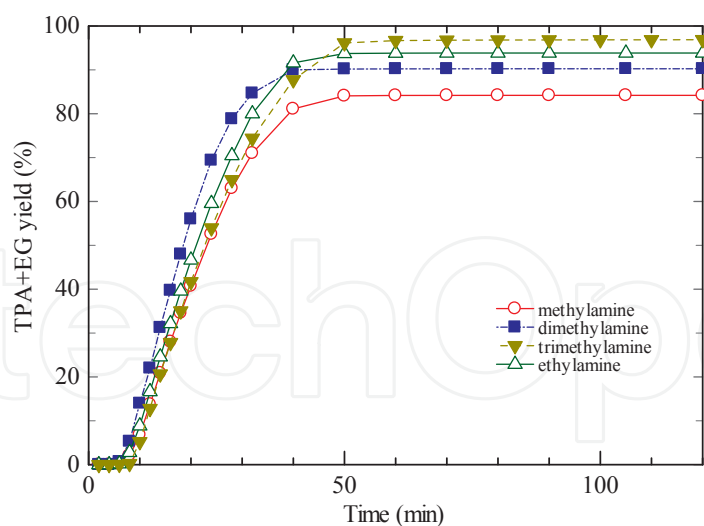


**Figure 7.** The effect of ammonia concentration on the reaction rate (slope) in plot of  $[(1-y)^{1/3}-1]$  vs. time at ammonia concentrations of 0.006, 0.06, 0.6 mol/kg, 493 K and solvent flow rate of 3 ml/min (set at ambient temperature) in a semi-batch reactor[11].

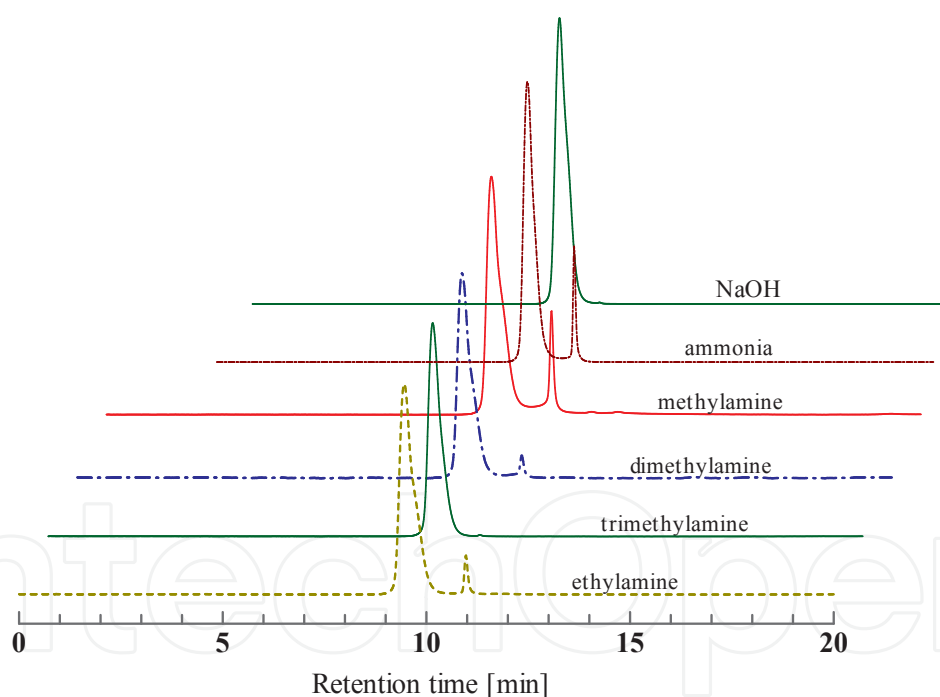


**Figure 8.** The effect of flow rates on the reaction rate (slope) in plot of  $[(1-y)^{1/3}-1]$  over flow time at solvent flow rates of 1, 3 and 5 ml/min (set at ambient temperature) and temperature of 493 K and 0.6 mol/kg ammonia concentration in a semi-batch reactor.

Various amines as well as ammonia are also effective for PET degradation. As seen in Figure 9, at 473 K and 10 MPa in a 0.6 mol/kg aqueous trimethylamine solution at a 3.0 mL/min solvent flow rate, the yields of TPA and EG for 50 min attained 77.6 and 18.6 %, respectively, close to the ideal values of 80 and 20%, respectively. Note that the final TPA+EG yields with trimethylamine were higher than those in methylamine, dimethylamine, and ethylamine. The yields decreased in the order of trimethylamine > ethylamine > dimethylamine > methylamine. The yields in trimethylamine and methylamine increased with flow time up to 30 min, but then those in methylamine were suppressed. This could be attributed to the intermediate products formed from the reactions between the amine and the polymer.

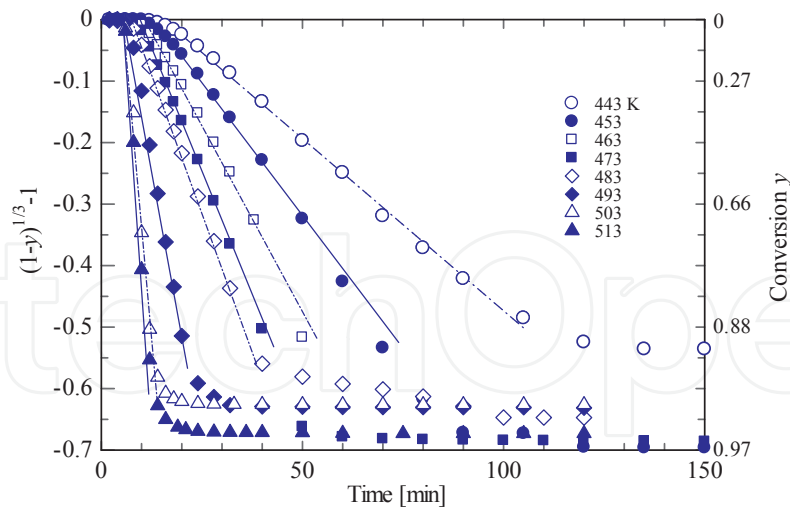


**Figure 9.** TPA+EG yields over flow time, in a 0.6 mol/kg aqueous solution of methylamine, dimethylamine, trimethylamine or ethylamine at a solvent flow rate of 3 mL/min, 473 K and 10 MPa in a semi-batch flow reactor [13].



**Figure 10.** HPLC chromatograms of product solutions with various amines, ammonia and NaOH at 473 K and concentrations of 0.6 mol/kg for 30 min [13].

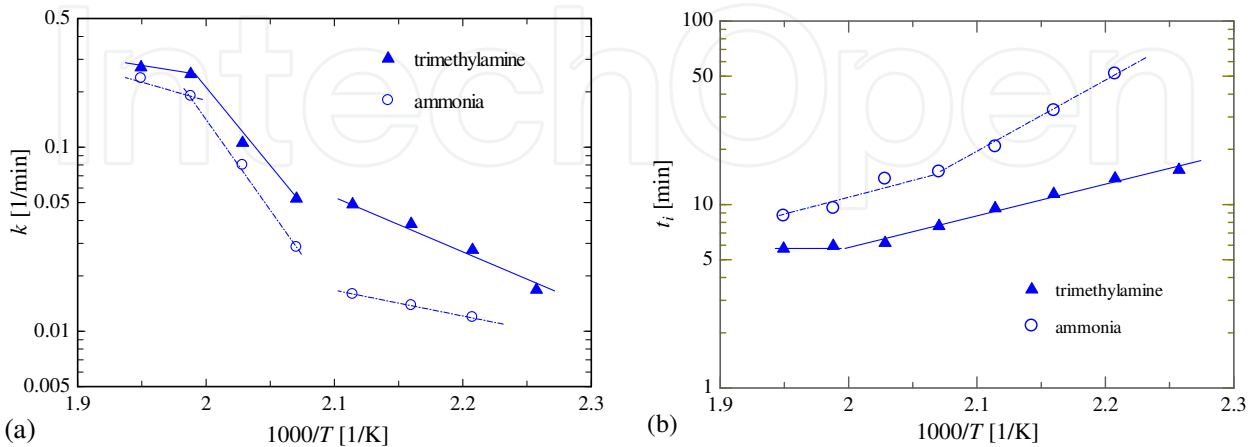
Figure 10 compares the HPLC chromatograms, monitored at 254 nm using the UV-Vis detector, of the product solutions, obtained in various aqueous solutions such as methylamine, dimethylamine, trimethylamine, ethylamine, ammonia or NaOH at 0.6 mol/kg concentration, 473 K and 10 MPa for 30 min. The highest peak in each chromatogram designated TPA and a smaller peak at a retention time of about 11 min was seen as a secondary product with



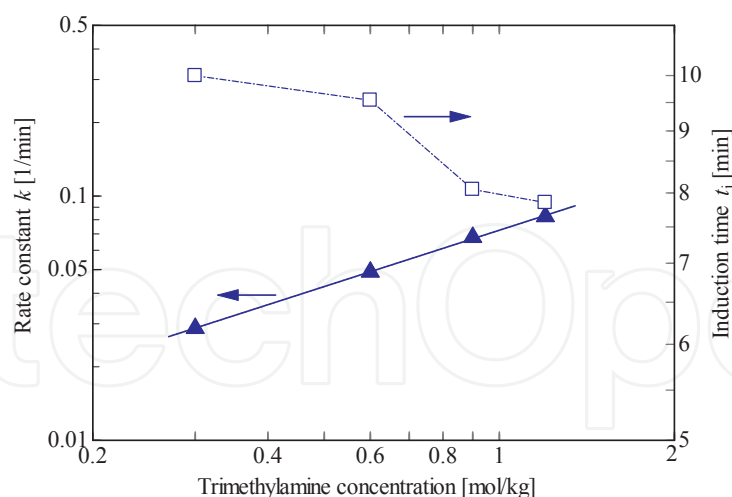
**Figure 11.** The validity of the surface reaction model in plot of  $[(1-y)^{1/3}-1]$  vs. flow time at temperatures from 443 to 513 K and 0.6 mol/kg trimethylamine concentration in a semi-batch reactor [13].

methylamine, ethylamine, dimethylamine and ammonia, whereas no peak appeared with NaOH and trimethylamine. It can be considered that the highest monomer yields with trimethylamine depended on the hydrolytic conversion of the amide compounds to the TPA, whose yields in terms of peak area ratio of the peak to TPA peak increased in the order of tertiary amide < secondary amide < primary amide.

Figure 11 shows the temperature dependences of plots  $[(1-y)^{1/3}-1]$  over flow time in a 0.6 mol/kg aqueous trimethylamine solution. As seen, the data are well represented by straight lines at all temperature studied over a nearly entire range of conversion  $y$ , up to those higher than 0.90. The induction time decreased with increasing reaction temperature, and the slope increased with increasing reaction temperature.



**Figure 12.** Arrhenius plots for (a) overall rate constants and (b) induction time as a function of  $1000/T$  for trimethylamine and ammonia at concentrations of 0.6 mol/kg [13].



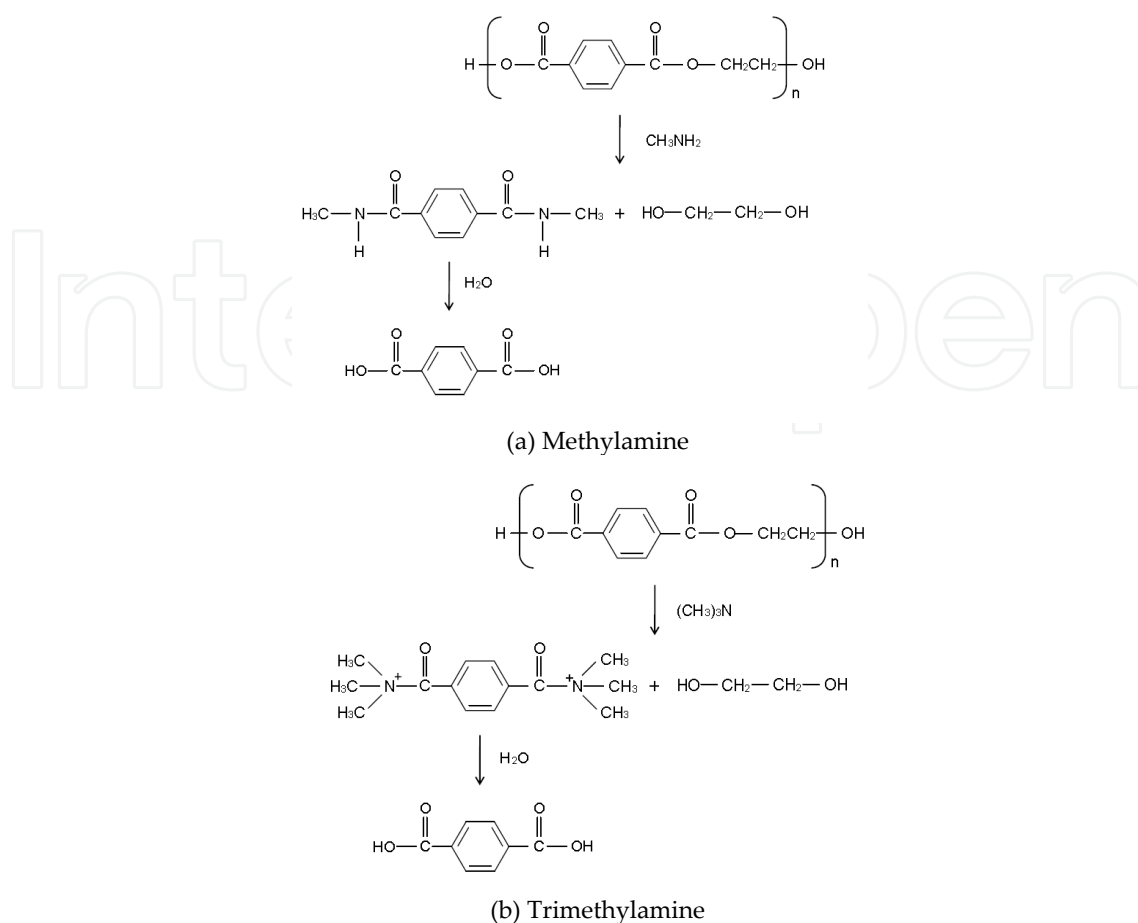
**Figure 13.** Effects of trimethylamine concentration on rate constant and induction time at 473 K and 10 MPa [13].

Temperature			
Additive	range(K)	$k_0$ (1/min)	$E$ (kJ/mol)
Trimethylamine	443 – 473	$3.34 \times 10^5$	61.7
	483 – 503	$5.42 \times 10^{15}$	157
Ammonia	453 – 473	$1.09 \times 10^1$	25.7
	483 – 503	$1.36 \times 10^{19}$	191

**Table 1.** Pre-exponential factors  $k_0$  and activation energies  $E$  for overall rate constants in 0.6 mol/kg aqueous trimethylamine and ammonia solutions [13].

Figure 12 shows an Arrhenius plot for (a) overall rate constants and (b) induction time determined at a 0.6 mol/kg trimethylamine concentration, as compared with those from a 0.6 mol/kg ammonia concentration. The activation energies and pre-exponential factors are listed in Table 1. The rates in aqueous solutions of both ammonia and trimethylamine were slow below 473 K, and the rate constants in trimethylamine were 2 to 3 times higher than those in ammonia. Around 480 K, the rates in both solutions increased, and then level off above 503 K. The values in trimethylamine were 1.3 to 2 times higher than those in ammonia at 483 to 503 K. Note that the reaction temperatures were lower than the melting point of the polymer. While the reason of the change in slopes is not known, the reaction involves some steps such as the polymer degradation, the decomposition of the intermediate products, and dissolution of the products, which may be affected by the reaction conditions.

The rate constants at 473 K and 10 MPa were correlated with the trimethylamine concentration, the slope of 0.766, as shown in Figure 13. The induction times were also correlated, but not with a straight line. This suggested that the overall reaction could be attributed to the nucleophilic reaction with amine, not to alkaline hydrolysis. The induction times decreased with increasing amine concentrations, but the effect of this is not clear.



**Figure 14.** Reaction scheme in aqueous (a) methylamine and (b) trimethylamine solutions [13].

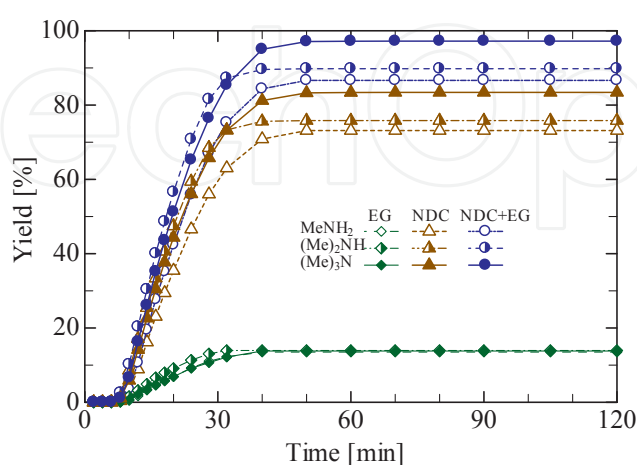
Figure 14 shows possible reaction schemes for two typical cases, in aqueous methylamine and trimethylamine solutions, where the intermediate product formed are relatively stable and readily decomposable, respectively. In the case of aqueous solutions of ammonia, and primary and secondary amine, their amides will be produced from attacking carbonyl carbons in PET polymers by their nitrogen atoms. While the amides could be mainly decomposed, some of them remain as by-products, as seen in Figure 10. In contrast, tertiary amine such as trimethylamine also attacks carbonyl carbons in PET polymers as ammonia, and primary and secondary amines do, but the amides so produced are readily converted to terephthalic acid under hydrothermal conditions due to the unstable intermediate having positive charge. Thus, to accomplish this stage the presence of water could be essential.

### 3.2. PEN

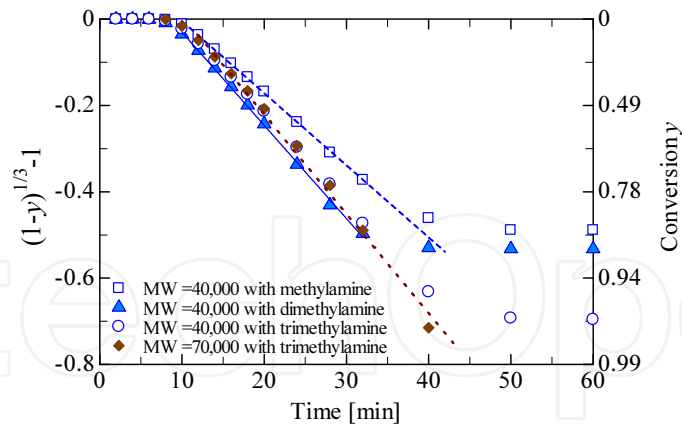
Figure 15 shows yields of NDC, EG and the sum of NDC and EG yields from PEN over time at 493 K and 5.0 MPa in 0.6 mol/kg aqueous solutions of trimethylamine, dimethylamine and methylamine. While the EG yields and the production rates are almost the same for the three amines, those of NDC are influenced by the amine species: The final NDC yield (83.4 % on carbon mass basis of initial PEN pellets) with trimethylamine is the highest, that (75.8 %) with

dimethylamine is lower, and that (73.1 %) with methylamine is the lowest. On the molar basis the NDC yields are 97.3, 88.5, 85.3 % ( $=100 \times \text{mol-NDC/mol-NDC unit in PEN}$ ) and the EG yields are 96.6, 97.7, 94.6 % ( $=100 \times \text{mol-EG/mol-EG unit in PEN}$ ) with trimethylamine, dimethylamine and methylamine, respectively. However, the formation rates in terms of slopes increase in the order of methylamine to trimethylamine to dimethylamine. The order is not coincident with that of the reactivity, i.e. methylamine > dimethylamine > trimethylamine. This may be influenced by other factors such as the molecular size of amine and the reactivity of intermediate compounds produced with NDC and each amine, as seen for PET with the three amines [13]. The intermediate products formed from reactions between PEN/degraded products and trimethylamine may be more readily converted to NDC than those with methylamine and dimethylamine. According to almost the same EG yields with the three amines, the reaction stages to form the intermediates with amine and EG are hardly affected with amine species.

Figure 16 validates the surface reaction model in Eq. (6) in plots of  $[(1-y)^{1/3} - 1]$  over time in the three aqueous solutions of amines such as trimethylamine, dimethylamine and methylamine for PEN with average molecular weight = 40,000, together with PEN with 70,000 in an aqueous trimethylamine solution, where all amine concentrations were 0.6 mol/kg at 493 K and 5.0 MPa. There are no significant differences in the rates between trimethylamine and dimethylamine, while the slope with methylamine is less steep. As seen in Fig. 15 the final NDC yield with methylamine was also the lowest among the three amines. It is interesting that the rates for PEN with MW = 70,000 and 40,000 were almost equal. The molecular weights of polymers did not influence the rates. Since solubility of NDC is low in the aqueous phase and the reaction temperature is lower than the melting point of PEN, oligomers may not be solubilized. The reaction may occur on the polymer surface, and the rate could be controlled not by degradation of polymers but by dissolution of NDC or decomposition reaction to produce NDC from intermediates, as seen for PET. In all the cases plots can be represented by the straight lines over a wide range of conversion  $y$ , up to  $y$  of 0.8, and Eq. (6) is found to be effective.



**Figure 15.** NDC, EG and NDC+EG yields over flow time at 493 K and 5.0 MPa with methylamine, dimethylamine and trimethylamine at 0.6 mol/kg concentration [14].



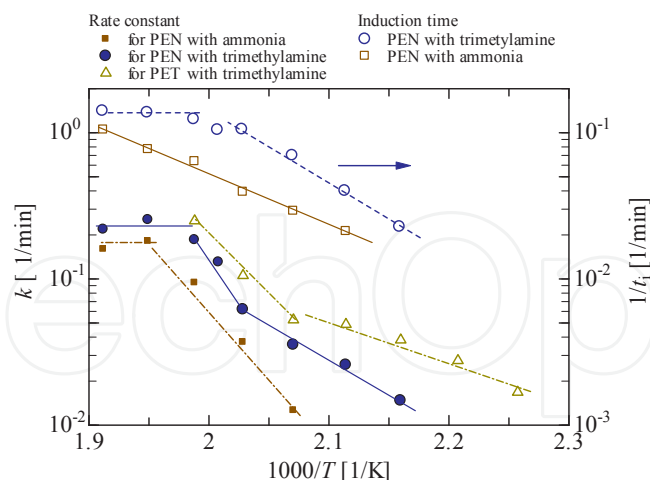
**Figure 16.** Effects of amine species on  $[(1-y)^{1/3} - 1]$  over flow time at 493 K and 5.0 MPa for PEN with average molecular weight = 40,000 in 0.6 mol/kg aqueous methylamine, dimethylamine, and trimethylamine solution, together with those for PEN with average molecular weight = 70,000 in 0.6 mol/kg aqueous trimethylamine solution [14].

Figure 17 shows Arrhenius plots for overall reaction rate constant  $k$  for PEN [14], as compared to those for PET [13] and PEN with ammonia [12], at amine and ammonia concentrations of 0.6 mol/kg, together with the reciprocal induction time  $1/t_i$  for PEN. The values of activation energy  $E$  and pre-exponential factor  $k_0$  in each stage for PEN with trimethylamine and ammonia are listed in Table 2. The temperature dependence of the reaction rates with trimethylamine are classified into the three stages in terms of slope as shown in Fig. 17: the moderately steep, and followed by the steeper, and almost the plateau, as observed for PET [13]. The transition temperature from the first to the second stage for PEN is higher than that for PET, and the rates for PET are higher than those for PEN. The transition temperature from the second to the plateau stage for PEN and PET are almost the same around 500 K. The reciprocal induction times also show the similar tendency in rate constants. Up to 503 K, the reciprocal values increase with decreasing  $1/T$  up to  $1.988 \times 10^{-3} \text{ 1/K}$  (503 K), and then show constants. Since the reciprocal values of induction times may be proportional to the rate constants [13], if the reactions behave as the first or zero-th order reaction kinetics, the values indicate the times which are required to be degraded to so low DP values as the polymers are soluble in the solution.

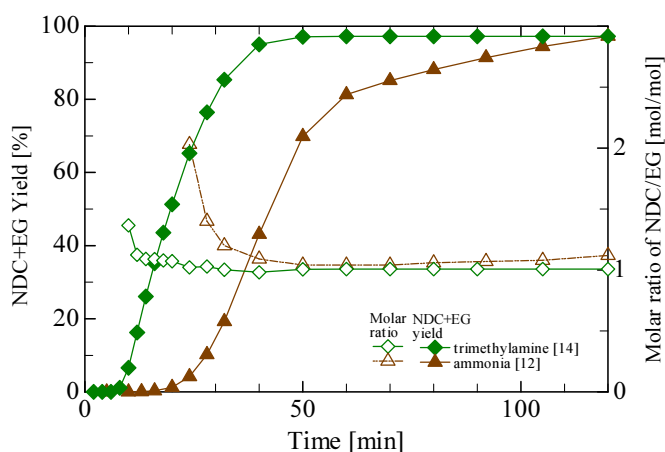
Additive	Temperature range [K]	$k_0$ [1/min]	$E$ [kJ/mol]
Trimethylamine	463 to 493	$1.19 \times 10^8$	87.8
	493 to 503	$6.26 \times 10^{22}$	226
	503 to 523	$k = 0.219 \text{ [1/min]}$	
Ammonia	473 to 513	$1.92 \times 10^{15}$	158
	513 to 553	$k = 0.185 \text{ [1/min]}$	

**Table 2.** Pre-exponential factor and activation energy in each stage for rate constants of PEN with trimethylamine [14] and ammonia [12] plotted in Fig. 16. (0.6 mol/kg aqueous trimethylamine at 5.0 MPa and ammonia solution at 10.0 MPa).





**Figure 17.** Arrhenius plots for overall rate constants for PEN [14] and PET [13] in 0.6 mol/kg aqueous trimethylamine solution, and for PEN [12] in 0.6 mol/kg aqueous ammonia solution, together with induction time  $t_i$  for PEN in 0.6 mol/kg aqueous trimethylamine solution [14], and in 0.6 mol/kg aqueous ammonia [12].



**Figure 18.** NDC+EG yields and molar yield ratio of NDC/EG over flow time at 493 K in 0.6 mol/kg aqueous trimethylamine [14] and 0.6 mol/kg ammonia [12] solutions. NDC+EG: solid key, NDC/EG: blank key.

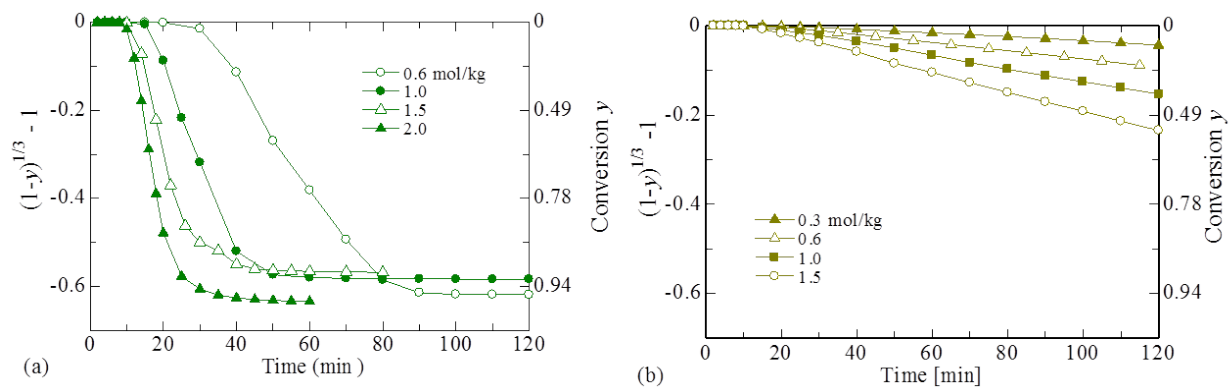
The  $k$  values for PEN with ammonia increased with increasing temperature, and above 503 K reached the plateau value, and were similar to that with trimethylamine. This can be considered to result from the mass transfer limitation. The reciprocal induction times with ammonia also increase with increasing temperature, and did not reach the plateau values. More reaction times are needed with ammonia due to lower reaction rates for degradation of molecular weights of PEN than those with trimethylamine.

Figure 18 compares the sum of NDC and EG yields and molar yield ratio of NDC/EG between ammonia and trimethylamine at 493 K and 0.6 mol/kg concentration of trimethylamine or ammonia. The production rate of NDC+EG with trimethylamine is much faster than that with ammonia. However, the final NDC+EG yields with both solutions reach nearly 100 %, and the molar yield ratio of NDC/EG are almost unity in major conversion periods, excluding the initial

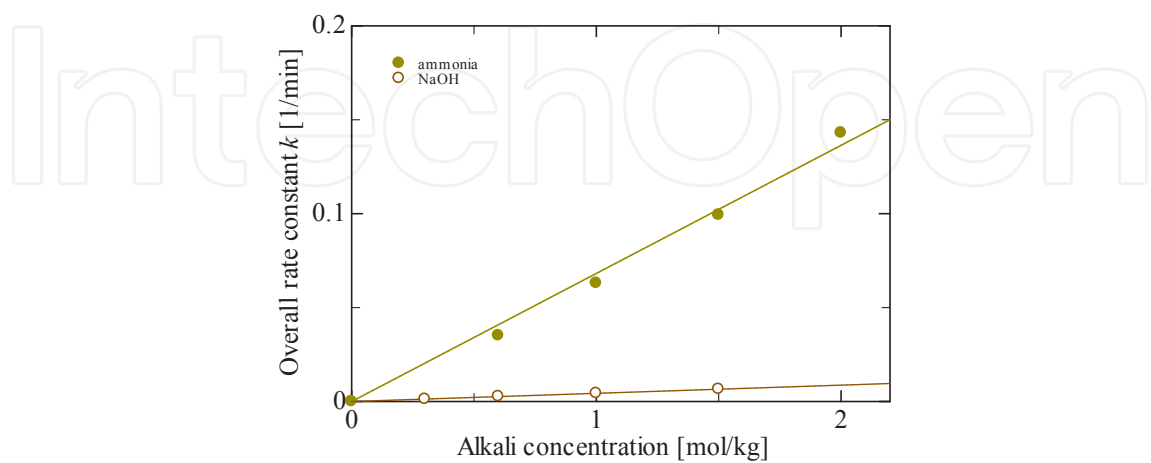
reaction periods, i.e. lower than product yields of 20 %. This suggests that the reaction to produce NDC initially took place, and followed by that to produce EG from intermediate products in either an aqueous trimethylamine or an aqueous ammonia solution.

3.3. PC

Figures 19(a) and (b) show the changes in  $[(1-y)^{1/3}-1]$  over time at various concentrations of (a) ammonia and (b) NaOH at a temperature of 433 K and a flow rate of 3 mL/min. In ammonia solution, each plot is expressed by approximately a straight line at each concentration over almost the entire range of conversion up to  $y > 0.9$ . In NaOH solution plots also show similar manner whereas the conversions are lower. The rates in both alkaline solutions increase with the concentration.



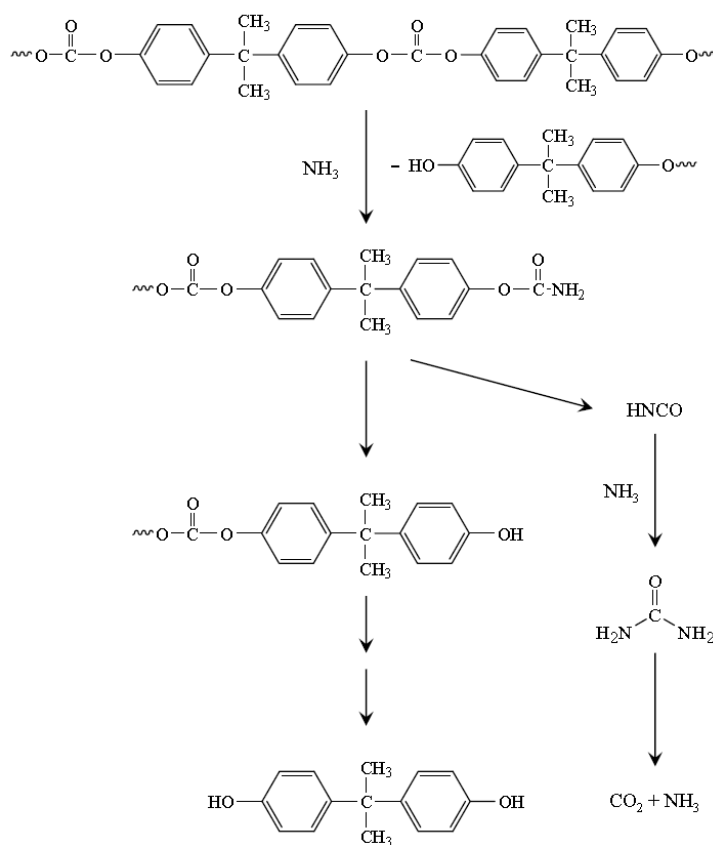
**Figure 19.**  $[(1-y)^{1/3} - 1]$  vs. flow time at various concentrations of (a) ammonia and (b) NaOH, at 433 K and 10 MPa in a semi-batch reactor [15].



**Figure 20.** Effects of alkali concentration on the overall rate constant at 433 K and 10 MPa with ammonia and NaOH in a semi-batch reactor [15].

Although the rates at various temperatures and ammonia/NaOH concentrations were well represented by Eq. (6), based on Eq. (4), in which the reaction rates were proportional to the surface area of PC pellets, the controlling step in the reaction was not determined. Since the activation energy with ammonia was not so high, the chemical reaction cannot be concluded to be controlling. Thus, the rate constant  $k$  in Eq. (6) is the overall value. The steps may consist of those in which the ammonia molecules are penetrated into polymer, those attack polymer, degraded components diffuse to the surface, and those dissolve into solution at pellet surfaces. The further studies are needed for clarifying the reaction mechanism and determining the controlling step.

The overall rate constants in both alkaline solutions at 433 K are plotted as a function of the alkaline concentration in Figure 20. Both the rate constants with ammonia and NaOH are proportional to the concentration, but the slope with ammonia is almost 15 times higher than that with NaOH. Note that there was no significant reaction with only water (no additives) at 433 K.



**Figure 21.** Reaction mechanism for conversion of polycarbonate to bisphenol A in aqueous ammonia solution under hydrothermal conditions [15].

The reaction mechanism shown in Figure 21 can be considered for the polycarbonate monomerization in an aqueous ammonia solution under hydrothermal condition. Carbonate

bonding in PC is decomposed by ammonolysis, and the carbamate ester is formed. The ester is further decomposed into isocyanate and polymers having bisphenol A termination. By repeating these steps polycarbonate is degraded to BPA. The isocyanate formed is further reacted with ammonia molecule to produce urea, and then the urea is decomposed to carbon dioxide and ammonia. The reaction steps are verified because no other major products were produced with the evidence that BPA yield was almost consistent with TOC in solution. The reaction steps for ammonolysis proposed by Mormann et al. [8] with supercritical ammonia is the same as that in the present study, but the latter steps for the conversion of isocyanate to urea, and the urea decomposition into carbon dioxide and ammonia are characteristic to reactions carried out in the aqueous solutions of ammonia and amines under hydrothermal conditions.

## 4. Conclusion

The presence of ammonia and amines is effective for conversion of polyesters and polycarbonate to the monomers in an aqueous solution under hydrothermal conditions at temperatures lower than melting points of polymer. The reaction rates for all polymers studied were expressed by the surface reaction model, i.e.  $2/3^{\text{rd}}$  order reaction kinetics with respect to unreacted mass of polymer. The reactivities of ammonia and amines tested are not dependent on the basicity, and the rates could be controlled by dissolution of intermediate products and/or monomers. The monomer yields with trimethylamine for PET and PEN, and those with methylamine for PC were nearly equal to the theoretical values. The aqueous solutions of ammonia and amine at low concentrations can be considered to be a promising medium for chemical recycling of polyesters and polycarbonates under hydrothermal conditions.

## Appendix

When polymer pellets are spherical, the initial polymer mass and that at time  $t$  are  $m_0$  and  $m$  [kg], respectively, the reaction rate, i.e. the decrease rate of  $m$  is assumed to be proportional to polymer surface area  $S$  [ $\text{m}^2$ ] with reaction rate constant  $k'$  [ $\text{kg}/(\text{min m}^2)$ ].

$$-\frac{dm}{dt} = k' S \quad (7)$$

The conversion  $y$  [-] is

$$y = 1 - \frac{m}{m_0} = 1 - \frac{\frac{4\pi R^3}{3} n \rho}{\frac{4\pi R_0^3}{3} n \rho} \quad (8)$$

where  $R_0$  and  $R$  are the particle radius of initial polymer and that at time  $t$ ,  $n$  is the number of particles in polymer mass  $m_0$  and  $\rho$  is the density of polymer. The rate is:

$$-\frac{dm}{dt} = m_0 \frac{dy}{dt} = k' (4\pi R^2) \frac{m_0}{\frac{4\pi R_0^3}{3} \rho}$$

$$\frac{dy}{dt} = \frac{3k'}{R_0 \rho} \left( \frac{R}{R_0} \right)^2 = k (1-y)^{2/3}$$

where  $k = 3k' / R_0 \rho$  [1/min].

## Author details

Toshitaka Funazukuri\*

Address all correspondence to: [tfunazo@kc.chuo-u.ac.jp](mailto:tfunazo@kc.chuo-u.ac.jp)

Department of Applied Chemistry, Chuo University, Kasuga, Bunkyo-ku, Tokyo, Japan

## References

- [1] Paszun, D., and T. Spychaj, *Ind. Eng. Chem. Res.*, 36, 1373-1383 (1997).
- [2] Yagihashi, M., and T. Funazukuri, *Ind. Eng. Chem. Res.*, 49, 1247-1251 (2010).
- [3] Farrow, G., D. A. S. Ravens, and I. M. Ward, *Polymer*, 3, 17-25 (1962).
- [4] Ellison, M. S., L. D. Fisher, K. W. Alger, and S. H. Zeronian, *J. Appl. Polym. Sci.*, 27, 247-257 (1982).
- [5] Awodi, Y. W., A. Johnson, R. H. Peters, and A. V. Popoola, *J. Appl. Polym. Sci.*, 33, 2503-2512 (1987).
- [6] Popoola, V. A., *J. Appl. Polym. Sci.* 36, 1677-1683 (1988).
- [7] Collins, M. J., S. H. Zeronian, and M. L. Marshall, *J. Macromol. Sci., Part A: Pure Appl. Chem.* A28, 775-792 (1991).
- [8] Mormann, W. H. Jung, and D. Spitzer, Ammonia as Reagent or Reaction Medium for Polymers, *In Supercritical Fluids as Solvents and Reaction Media*, Brunner, G. Eds.; Elsevier: Amsterdam, 2004; pp. 593-616.

- [9] Zenda, K., and T. Funazukuri, Joint 8th Int. Symp. on Hydrothermal Reactions and 7th Int. Conf. on Solvo-Thermal Reactions, Aug, Sendai, Japan (2006).
- [10] Zenda, K., K. Hatakeyama, R. Arai, and T. Funazukuri, Proc. of Super Green 2007, The 5th Int. Conf. on Supercritical Fluids, Nov. Seoul, Korea (2007).
- [11] Zenda, K., and T. Funazukuri, *J. Chem. Technol. Biotechnol.*, 83, 1381-1386 (2008).
- [12] Arai, R., K. Zenda, K. Hatakeyama, K. Yui, and T. Funazukuri, *Chem. Eng. Sci.*, 65, 36-41 (2010).
- [13] Wakabayashi, N., T. Kojima, and T. Funazukuri, *Ind. Eng. Chem. Res.*, 51, 5699-5704 (2012).
- [14] Wakabayashi, N., M. Taguchi, and T. Funazukuri, *J. Chem. Eng. Jpn*, 47, 908-913 (2014).
- [15] Hatakeyama, K., T. Kojima, and T. Funazukuri, *J. Mater. Cycles Waste Manag.*, 16, 124-130 (2014).
- [16] JSME (Japan Society of Mechanical Engineers) Steam Tables Based on IAPWS-IF97 (International Association for the Properties of Water and Steam International Formulation 1997 for the Thermodynamic Properties of Water and Steam) 5th ed, JSME, Tokyo, 1999.