Communication

Depolymerization of PET with *n*-Hexylamine, *n*-Octylamine, and with 3-Amino-1-Propanol Affording Terephthalamides

Sumiho Hiruba , Yohei Ogiwara , Kotohiro Nomura *

Posted Date: 7 January 2025

doi: 10.20944/preprints202501.0484.v1

Keywords: PET; depolymerization; aminolysis; terephthalamide; chemical recycling; upcycling; poly(ethylene terephthalate); titanium catalyst; homogeneous catalysis

Communication

Depolymerization of PET with *n*-Hexylamine, *n*-Octylamine, and with 3-Amino-1-Propanol Affording Terephthalamides

Sumiho Hiruba [1], Yohei Ogiwara [2] and Kotohiro Nomura [1,*]

[1] Department of Chemistry, Tokyo Metropolitan University, 1-1 Minami Osawa, Hachioji, Tokyo 192-0397, Japan
[2] Department of Chemistry and Biomolecular Science, Gifu University, 1-1 Yanagido, Gifu, Gifu 501-1193, Japan
* Correspondence: ktnomura@tmu.ac.jp

Abstract: Chemical conversion of plastic waste has been considered as important subject in terms of circular economy, and chemical recycling and upcycling of poly(ethylene terephthalate) (PET) has been considered as one of the important subjects. In this study, depolymerization of PET with *n*-hexylamine, *n*-octylamine, and with 3-amino-1-propanol have been explored in the presence of Cp*$TiCl_3$ (Cp* = C_5Me_5). The reactions of PET with *n*-hexylamine, *n*-octylamine at 130 °C afforded the corresponding di(*n*-alkyl) terephthalamides in high yields (>90 %), and Cp*$TiCl_3$ plays a role as the catalyst to facilitate the conversion in the exclusive selectivity. The reaction of PET with 3-amino-1-propanol proceeded at 100 °C even in the absence of Ti catalyst, affording bis(3-hydroxy) terephthalamide in high yields. Unique contrast in the depolymerization of PET between by transesterification with alcohol and by aminolysis has been demonstrated.

Keywords: PET; depolymerization; aminolysis; terephthalamide; chemical recycling; upcycling; poly(ethylene terephthalate); titanium catalyst; homogeneous catalysis

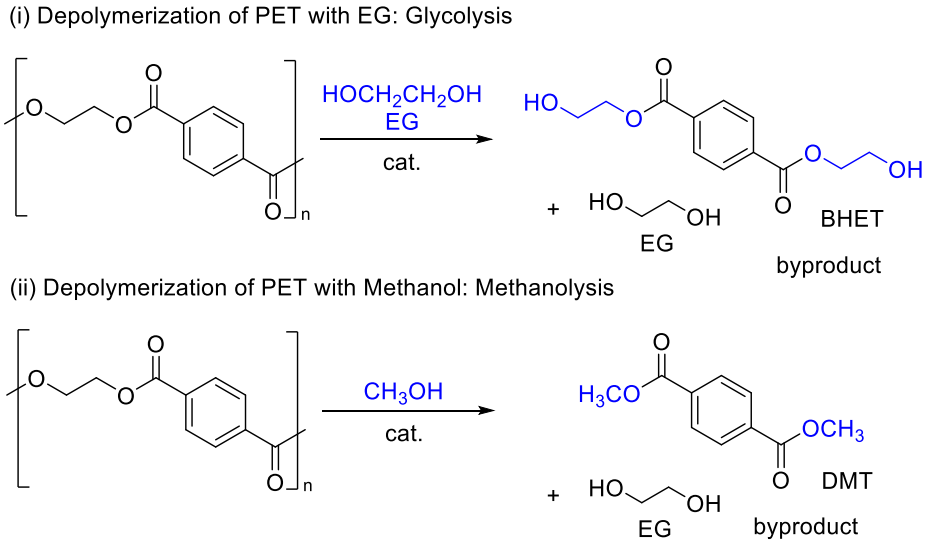
1. Introduction

The importance of chemical conversion of plastic waste such as chemical recycling (conversion to monomers), upcycling (conversion to value-added chemicals) has been pronounced in terms of circular economy [1–4]. Poly(ethylene terephthalate) (PET) has been a commodity plastic used as drink bottles, clothes, carpets etc. in our daily life, and mechanical recycling of PET bottle (collection, sorting, and re-processing after purification steps) has been known. Recently, in terms of carbon neutral concept as well as circular economy, chemical recycling of polyesters [5–10] including PET [10–15] has been recognized as the important technology for the purpose [1–15]. Since recycled PET resin through the above mechanical recycling has certation limitation due to their inferior quality, there are many studies concerning the chemical recycling, depolymerization of PET to monomers that are eventually converted to fresh resin which should be equivalent to the petroleum-derived one [12–43].

As shown in Scheme 1, there are two major methods for depolymerization of PET with ethylene glycol (EG) to afford bis(2-hydroxyethyl)terephthalate (BHET, so-called glycolysis process) or methanol to afford dimethyl terephthalate (DMT, called methanolysis). For example, (i) glycolysis by using a catalyst system consisting of $Zn(OAc)_2$—Na_2CO_3 (at 196 °C) [22] or $Zn(OAc)_2$—1,3-dimethylurea (at 190 °C) [27], or a certain combination of acids and base (5 mol%, 180 °C) [31], (ii) methanolysis under high temperature (e.g., 280–310 °C) and high-pressure conditions (ca. 4 MPa, the addition of K_2CO_3 reduced the harsh conditions) [10-12] have been known. Another method for the depolymerization of PET with *n*-butanol in the presence of $[HO_3S\text{-}(CH_2)_3\text{-}NEt_3]Cl$–$ZnCl_2$ at 205 °C [26] have also been known. As described above, most of methods reported [16–39,43], however, require harsh conditions (high temperature, pressure) and/or excess base, acids, and/or inorganic

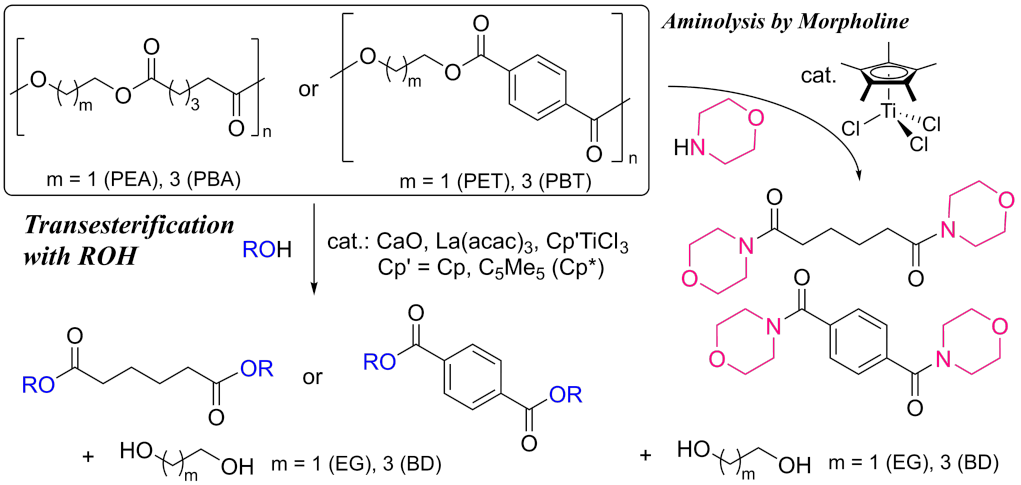
 doi:10.20944/preprints202501.0484.v1

salts. The process consists of depolymerization, decolorization, deionization (removal of salt), crystallization (initial purification), solid-liquid separation, concentration and vacuum distillation [10–15]. The methods, however, often face difficulty such as separation of byproduct (diethylene glycol etc.) and/or careful removal of inorganic salts (severe impurities in the final purification step by vacuum distillation upon heating) [10–15]. Therefore, development of the acid-, base-free depolymerization methods have been considered as the important technology especially in terms of simple purification process as well as of the sustainable process (total atom efficiency, no inorganic effluents, waste waters etc.).



Scheme 1. Conventional Methods for Depolymerization of PET.

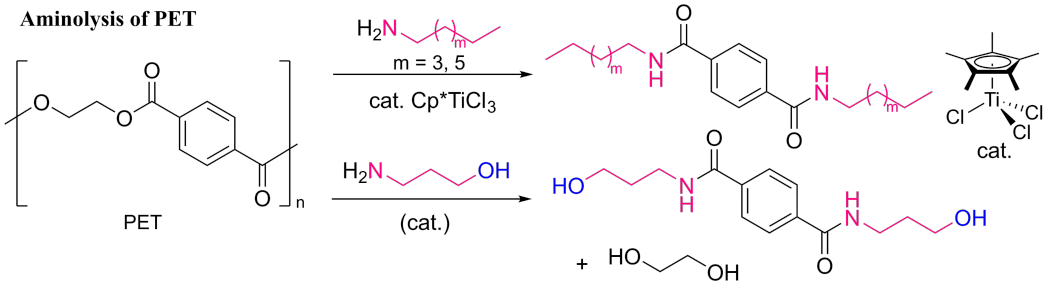
More recently, acid-, base-free depolymerization of PET [40–42] as well as conventional polyesters [44–47] with alcohols have been demonstrated in the presence of $La(acac)_3$ (acac = acetylacetonato) [40,46], CaO [42,45], or $Cp'TiCl_3$ (Cp' = Cp, Cp*) [41,44]. Moreover, $FeCl_3$ catalyzed depolymerization not only PET bottles, but also textile wastes consisting of PET with ethanol has been demonstrated [47]. These depolymerization, transesterification with alcohols (ethanol, methanol, cyclohexane methanol etc.), afforded the corresponding monomers exclusively (Scheme 2, >99% conversion, >99% selectivity). We also reported that PET was treated with morpholine in the presence of Cp^*TiCl_3 to give the corresponding amide in high yields [48].



Scheme 2. Catalytic depolymerization of polyesters with alcohols and morpholine.

 doi:10.20944/preprints202501.0484.v1

In this paper, we thus present reactions of PET with linear *n*-alkylamines such as *n*-hexylamine, *n*-octylamine, and 3-amino-1-propanol to expand the utility of this developed methods for the efficient upcycling of the PET waste. Through this research, we wish to provide a difference in depolymerization of polyesters between by the transesterification and by the aminolysis; the reaction of PET with 3-amino-1-propanol occurred exclusively with the amino group to afford the corresponding bis(3-hydroxypropyl) terephthalamide, 1,4-[$HOCH_2CH_2CH_2N$-C(O)]$_2C_6H_4$, even in the absence of catalyst (Scheme 3).

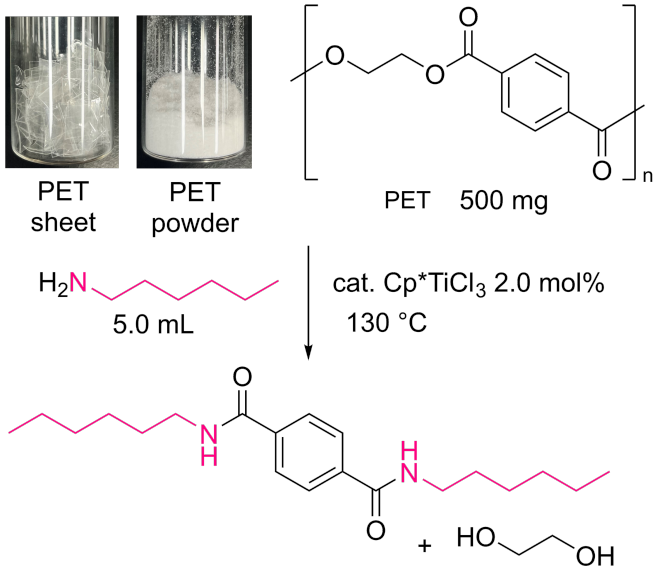


Scheme 3. Catalytic depolymerization of PET with *n*-hexylamine, *n*-octylamine, and with 3-amino-1-propanol (this study).

2. Results and Discussion

2.1. Reactions of PET with n-Hexylamine, n-Octylamine

Reactions of PET with *n*-hexylamine were conducted using a sealed tube in the presence of Cp^*TiCl_3 catalyst (2.0 mol% to the monomer unit of PET) at 130 °C (set into the alumina heating blocks of the parallel reactor) on the basis of the conditions for depolymerization with morpholine [48] (Scheme 4, details are described in the Experimental section). After the reaction, the reaction mixture was placed *in vacuo* to remove volatiles, and the resultant mixture was further purified with chloroform to isolate the product, di(*n*-hexyl) terephthalamide, by recrystallization. Samples of PET sheet, prepared by cutting the PET drink bottle, or PET powder, prepared from the commercially available fresh resin by using a grinding machine, were used in this study. The results conducted under various conditions are summarized in Table 1.



Scheme 4. Depolymerization of PET with *n*-hexylamine.

As shown in Figure 1, ^{1}H- and ^{13}C-NMR spectra, the reaction product, isolated as white solids, was di(*n*-hexyl) terephthalamide as a pure form especially when the reaction was conducted for 48 h

 doi:10.20944/preprints202501.0484.v1

(runs 1,2). As shown in Figure S1a in Supplementary Materials (SM), the ^{1}H NMR spectrum (in tetrachloroethane-d_2) of the reaction mixture after removal of volatiles shows that the observed resonances were assigned as the desired products, suggesting that the reaction proceeded exclusively in this catalysis. It seems that the reactions completed after 16 h (runs 3,4), since the products yields isolated were already high (runs 3,4), very close to those conducted after 48 h (runs 1,2). As observed in the transesterification of PET with ethanol [41,47], the catalyst performances were not strongly affected by the nature of PET samples (sheet or powder, runs 1-4).

Table 1. Depolymerization of PET with *n*-hexylamine catalyzed by Cp*TiCl$_3$.[1]

run	PET[2]	cat. / mol%	temp. / ºC	time / h	yield[3] / mg	/ %
1	sheet	2.0	130	48	786	91
2	powder	2.0	130	48	820	95
3	sheet	2.0	130	16	789	91
4	powder	2.0	130	16	794	92
5	sheet	2.0	130	6	766	89
6	powder	2.0	130	6	732	85
7	powder	0	130	6	714	83
8	powder	2.0	100	6	408	47
9	powder	5.0	100	6	498	58

[1] Conditions: PET (500 mg, 2.60 mmol, repeating unit), Ti 0 - 5.0 mol%, *n*-hexylamine 5.0 mL. [2]PET sheet cut by drink bottle or grounded powder (Scheme 4). [3]Isolated yield by recrystallization from ethanol.

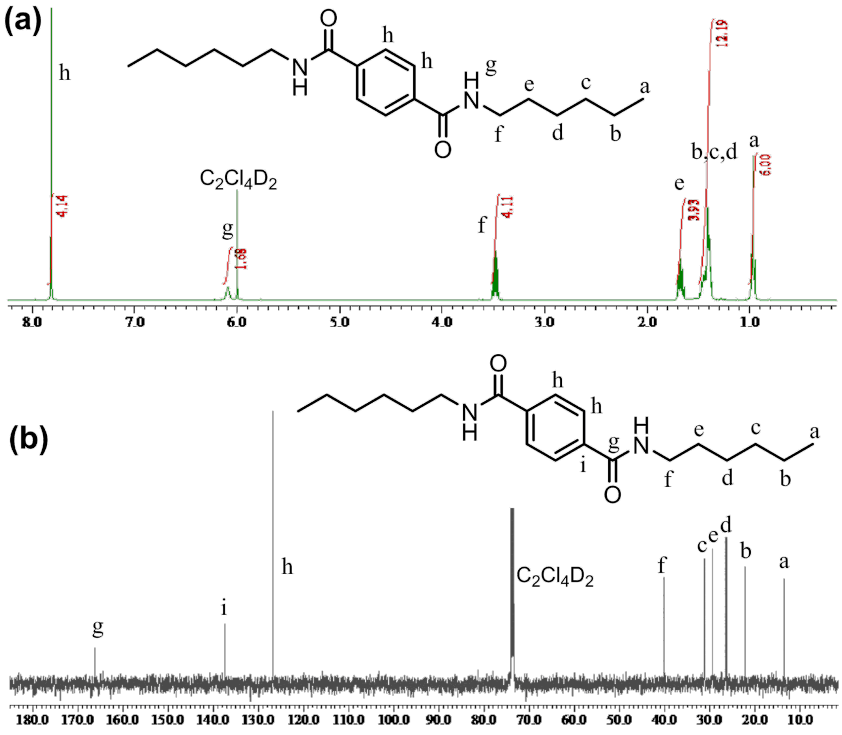


Figure 1. (a) ^{1}H-NMR spectrum and (b) ^{13}C-NMR spectrum for di(*n*-hexyl) terephthalamide (in tetrachloroethane-d_2 at 100 °C).

In contrast, resonances at δ = 4.73 and 8.13 ppm were observed in addition to the terephthalamide in the ^{1}H NMR spectrum of the reaction mixture after 6 h (run 6, Figure 2b). Interestingly, the reaction also proceeded in the absence of Cp*TiCl$_3$ (run 7, Figure 2c), but the intensities of the additional peaks were apparently high. These resonances became decreasing upon increasing the catalyst (Ti 3.0 and 5.0, respectively, Figure S1, SM). These resonances disappeared

 doi:10.20944/preprints202501.0484.v1

when the reaction mixture was passing through a Celite Pad before recrystallization; this caused a difficulty for identification of the byproduct by GC, GC-MS. In order to isolate the intermediate, the reactions were conducted at 100 ºC in the presence of Cp*TiCl$_3$ (runs 8,9), and the byproduct was precipitated from the reaction mixture by addition of methanol. On the basis of NMR spectra (Figures 2d,e) and DSC thermogram of the resultant solid, the melting temperature (237 ºC) was relatively close to that in PET (244.8 C, Figure S2 in SM). It thus seems likely that these resonances are due to PET oligomers (although we were not able to measure the molecular weight due to their insolubility in THF nor chloroform even for the GPC measurement). The results clearly explain that the PET was depolymerized to PET oligomers and gradually converted to the corresponding to terephthalamide, as observed in the depolymerization with alcohols by transesterification [41,42]. These results also clearly indicate that Cp*TiCl$_3$ play a role as the catalyst that facilitates the aminolysis under these conditions.

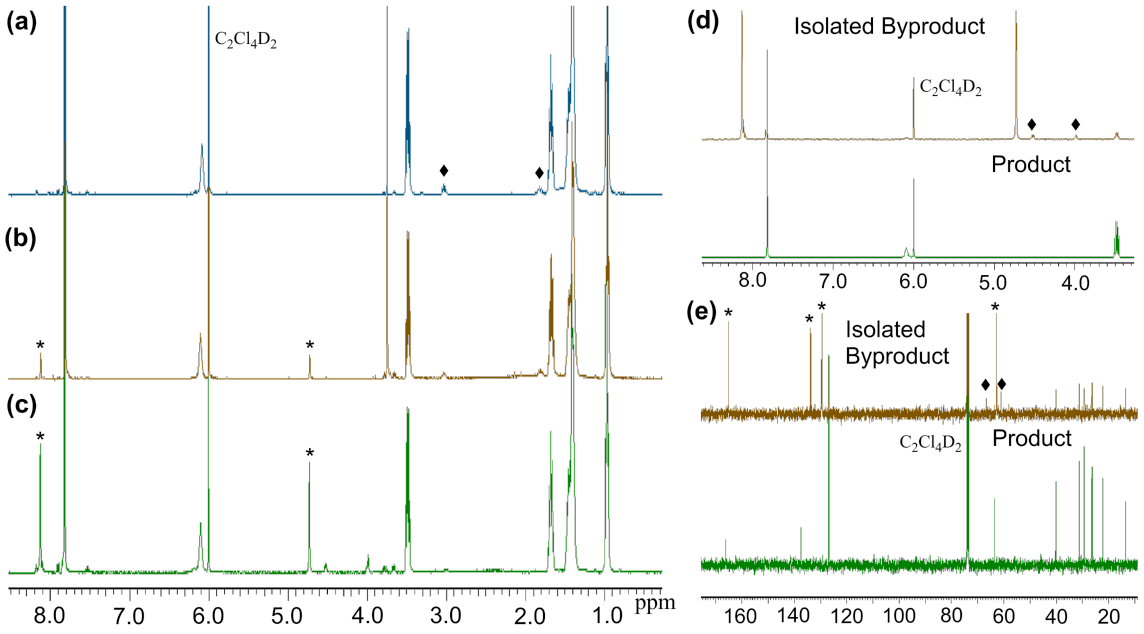


Figure 2. (a)-(c) ^{1}H NMR spectra of the reaction mixture (after removal of volatiles) in the reaction of PET with *n*-hexylamine (130 ºC, 6 h) in the presence of 2.0 mol% Cp*TiCl$_3$ (a) after 48h (run 2). (b) 6 h (run 6), and (c) after 6 h in the absence of catalyst (run 7). (d) ^{1}H-NMR spectrum and (e) ^{13}C NMR spectra (in tetreachloroethane-*d*$_2$ at 100 ºC) for isolated byproduct (PET oligomer) separated from the reaction mixture conducted at 100 ºC (runs 8,9). Resonances marked with * were corresponded to byproduct (PET oligomers) and peaks marked with ♦ are impurities.

Similarly, reactions of PET with *n*-octylamine were conducted at 130 ºC in the presence of Cp*TiCl$_3$ (2.0 mol%), and the results are summarized in Table 2. The reactions afforded the corresponding amide, di(*n*-octyl) terephalamide, exclusively without contamination of the other byproduct, as shown in Figure S3 (NMR spectra) in SM. Compared to the reaction with *n*-hexylamine, isolation of the *n*-octylamide seemed rather difficult due to difficulty of removing *n*-octylamine *in vacuo* and the product by repetitive washing with chloroform was thus necessary to remove the amine completely. As observed in the transesterification of PET with ethanol [41,47] as well as in the reactions with *n*-hexylamine (Table 1), the catalyst performances were not strongly affected by the nature of PET samples (sheet or powder, runs 10,11). As shown in Figure S4 (SM), the isolated product contained impurity (PET oligomer) in trance amount in the ^{1}H NMR spectrum (reaction 16 h); it thus seems that longer reaction time was necessary for obtainment of the terephthalamide in the exclusive yield.

 doi:10.20944/preprints202501.0484.v1

Table 2. Depolymerization of PET with *n*-octylamine catalyzed by Cp*$TiCl_3$.[1]

run	PET[2]	cat. / mol%	temp. / ºC	time / h	yield[3] / mg	/ %
10	sheet	2.0	130	48	935	93
11	powder	2.0	130	48	929	92
12	powder	2.0	130	16	904	90*
13	powder	2.0	130	6	694	69

[1] Conditions: PET (500 mg, 2.60 mmol, repeating unit), Ti 2.0 mol%, *n*-octylamine 5.0 mL. [2]PET sheet cut by drink bottle or grounded powder (Scheme 4). [3]Isolated yield by recrystallization from toluene. *Trace amount of PET oligomer contaminated (by ^{1}H NMR spectrum, Figure S4, SM).

2.2. Reaction of PET with 3-Amino-1-Propanol

Reactions of PET with 3-amino-1-propanol were conducted at 100 or 130 ºC in the presence/absence of Cp*$TiCl_3$ catalyst, and the results are summarized in Table 3. It was revealed that the reaction product was bis(3-hydroxy) terephthalamide, 1,4-[$HOCH_2CH_2CH_2NC(O)$]C_6H_4, exclusively as shown in Figure 3 (^{13}C NMR spectrum) as well as Figure S5, SM. The pure isolation of the amide seemed rather difficult because of separation of the product with 3-amino-1-propanol remained even after removal of volatiles *in vacuo*. Therefore, repetitive precipitation with chloroform was required (reason for rather low yields compared to those in the reaction with *n*-hexylamine). Reason for exclusive obtainment of amide instead of ester would be due to a stability of the product (amide is more stable thermodynamically compared to esters).

It should be noted that the reactions completed without catalyst and the yields in the absence of Ti catalyst were highly close to those in the presence of Ti catalyst. Moreover, no significant differences were seen when the reactions were conducted at 100 ºC after 3 h (run 17 vs run 21). The reactions were rather affected by the temperature employed, since the reaction mixture conducted at 80 ºC remained PET slurry after 6 h (runs 18,22).

Table 3. Depolymerization of PET with 3-amino-1propanol catalyzed by Cp*$TiCl_3$.[1]

run	cat. / mol%	temp. / ºC	time / h	yield[2] / mg	/ %
14	2.0	130	24	616	84
15	2.0	100	24	646	89
16	2.0	100	6	662	91
17	2.0	100	3	645	88
18	2.0	80	6	528	72*
19	0	100	24	660	91
20	0	100	6	660	91
21	0	100	3	644	88
22	0	80	6	516	71*

[1] Conditions: PET powder grounded (500 mg, 2.60 mmol, repeating unit), Ti 0 or 2.0 mol%, 3-amino-1-propanol amine 5.0 mL. [2]Isolated yield by precipitation with chloroform. *The reaction mixtures were heterogeneous containing PET slurry.

 doi:10.20944/preprints202501.0484.v1

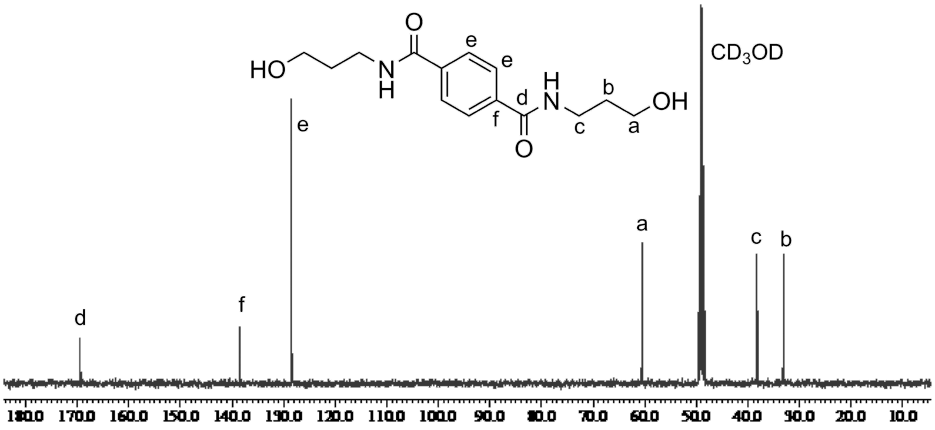


Figure 3. ^{13}C NMR spectrum for bis(3-hydroxypropyl) terephthalamide (in methanol-d_4 at 25 ℃).

3. Materials and Methods

All experiments were conducted under a nitrogen atmosphere using a glove box. $CpTiCl_3$, Cp^*TiCl_3 (Tokyo Chemical Industry, Co., Ltd., Tokyo, Japan), n-hexylamine, n-octylamine, and 3-amino-1-propanol (Tokyo Chemical Industry, Co., Ltd., Tokyo, Japan) were used as received. Poly(ethylene terephthalate (PET) resin (IV = 0.80 ± 0.02 dL/g) were received from companies (by donation for research purpose only), and were used as PET powers after griding using 0.25 mm mesh using grinding machine. PET sheets were prepared by cutting the PET drink bottle. All ^{1}H and ^{13}C{^{1}H} NMR spectra (in tetrachloroethane-d_2 at 100 °C or methanol-d_4 at 25 ℃) were measured on a JEOL JNM ECS400 spectrometer (399.8 MHz for ^{1}H and 100.5 MHz for ^{13}C, JEOL Ltd., Tokyo, Japan) using $SiMe_4$ as the reference at 0.00 ppm (chemical shifts were reported in parts per million).

General procedure for reaction of poly(ethylene terephthalate (PET) with amines. An oven-dried reaction apparatus (100 mL scale screw-cap glass tube) was charged with the prescribed amount of $CpTiCl_3$, 500 mg of PET (powder or sheet, shown in Scheme 4), and 5.0 mL of amine (*n*-hexylamine, *n*-octylamine, or 3-aminopropanol) under a nitrogen atmosphere. The reaction mixture was stirred at prescribed temperature using an alumina heating blocks in parallel reaction apparatus (ChemiStation™, Tokyo Rikakikai Co., Ltd., PPS-2511). After the reaction, the mixture was cooled to room temperature and transferred to a round-bottom flask for removal of volatiles, and the products, terephthalamide, were isolated by precipitation or recrystallization by ethanol or toluene. The reaction mixture containing impurities (PET oligomer) was separated by filtration using Celite pad after dissolving the products by chloroform-methanol mixed solution.

Di(*n*-hexyl) terephthalamide: ^{1}H NMR (tetrachloroethane-d_2): δ 7.82 (s, 4H, Ar-H), 6.09 (s, 2H, -NH-), 3.48 (q, J = 6.8 Hz, 4H, -NHC$\underline{H_2}$-), 1.71-1.64 (m, 4H, -NHCH$_2$C$\underline{H_2}$-), 1.47-1.37 (m, 12H, -CH$_2$-), 0.97 (t, J = 7.1 Hz, 6H, -CH$_3$). ^{13}C{^{1}H} NMR (tetrachloroethane-d_2): δ 166.2(-CO-), 137.4 (Ar), 126.9 (Ar), 40.2, 31.2, 29.5, 26.4, 22.2, 13.6.

Di(*n*-octyl) terephthalamide: ^{1}H NMR (tetrachloroethane-d_2): δ 7.82 (s, 4H, Ar-H), 6.06 (s, 2H, -NH-), 3.49 (q, J = 6.7 Hz, 4H, -NHC$\underline{H_2}$-), 1.71-1.64 (m, 4H, -NHCH$_2$C$\underline{H_2}$-), 1.47-1.35 (m, 20H, -CH$_2$-), 0.95 (t, J = 6.9 Hz, 6H, -CH$_3$). ^{13}C{^{1}H} NMR (tetrachloroethane-d_2): δ 166.2 (-CO-), 137.4 (Ar), 126.9 (Ar), 40.2, 31.5, 29.5, 29.0, 28.9, 26.8, 22.3, 13.7.

Di(3-hydroxypropyl) terephthalamide: ^{1}H NMR (DMSO-d_6): δ 8.56 (t, J = 5.5 Hz, 2H, -NH-), 7.89 (s, 4H, Ar-H), 4.50 (t, J = 5.0 Hz, 2H, -OH), 3.46 (q, J = 6.0 Hz, 4H, -C$\underline{H_2}$OH-), 3.32 (q, J = 6.5 Hz, 4H, -NHC$\underline{H_2}$-), 1.71-1.65 (m, 4H, -CH$_2$-). ^{13}C{^{1}H} NMR (methanol-d_4): δ 169.4 (-CO-), 138.4 (Ar), 128.4 (Ar), 60.6 (-CH$_2$OH), 38.2(-NHCH$_2$-), 33.2(-CH$_2$-).

4. Conclusions

As described in the introduction, conversions of PET into fine chemicals called upcycling have been one of the important key technologies in terms of establishment of circular economy. We have

 doi:10.20944/preprints202501.0484.v1

demonstrated preparations of three amides in the depolymerization of PET with *n*-hexylamine, *n*-octylamine and with 3-amino-1-propanol, affording the corresponding terephthalamides in high yields (without by-production of side products). Cp*$TiCl_3$, the effective catalyst for aminolysis of PET with morphoiline [48] plays a role to facilitate the reaction but these reactions proceeded even in the absence of Ti catalyst. Indeed, no significant differences in the product yields were observed in the depolymerization of PET with 3-amino-1-propanol affording the corresponding bis(3-hydroxy) terephthalamide in high yields even at 100 ℃. The results are significant contrast to those in the depolymerization with alcohols by transesterification, because presence of Cp'$TiCl_3$ (Cp' = Cp, Cp*) was prerequisite to proceed the reaction as catalyst. The difference would be probably explained as due to the stability of the product, amide, thermodynamically compared to esters, as well as amine would probably play a role as catalyst in the aminolysis of PET, on the basis of results in the depolymerization with 3-amino-1-propanol. Since the method could be effective for chemical conversion of the other PET wastes (textile waste), as demonstrated previously [47]. The observed fact should be potentially important for catalytic chemical conversion of polyester to fine chemicals. We shall explore more possibilities with various polyesters and will introduce in the near future.

Supplementary Materials: The following supporting information can be downloaded at the website of this paper posted on Preprints.org. Figures S1-S5, Additional NMR spectra for reaction mixture in the depolymerization of PET with *n*-hexylamine, *n*-otylamine, and di(n-octyl) terephthalamide and bis(3-hydroxy) terephthalamide, and DSC thermograms of isolated byproduct (PET oligomer) in the reaction of PET with *n*-hexylamine.

Author Contributions: Conceptualization, K.N.; methodology, K.N.; validation, formal analysis, S.H.; investigation, data curation, K.N. and S.H.; resources, K.N. and Y.O.; writing—original draft preparation, S.H. and K.N.; writing—review and editing, visualization, supervision, project administration, funding acquisition, K.N. All authors have read and agreed to the published version of the manuscript.

Funding: This project was partly supported by JST-CREST (Grant Number JPMJCR21L5).

Data Availability Statement: The data are contained within the article and the Supplementary Material (NMR spectra, DSC thermograms).

Acknowledgments: KN expresses his thanks to Prof. Masafumi Hirano (Tokyo Univ. A&T) and the laboratory members for fruitful discussion. K.N. and S.H. also express their thanks to Dr. Hiroshi Hirano (Osaka Institute of Industrial Science) for preparation of PET powders from the resin employed in this study.

Conflicts of Interest: The authors declare no conflicts of interest.

References

1. Coates, G.W.; Getzler, Y.D.Y.L. Chemical recycling to monomer for an ideal, circular polymer economy. *Nat. Rev. Mat*. **2020**, *5*, 501–516. doi.org/10.1038/s41578-020-0190-4
2. Collias, D.I.; James, M.I.; Layman, J.M. (Eds.) *Circular Economy of Polymers: Topics in Recycling Technologies*; ACS Symposium Series; American Chemical Society: Washington, DC, USA, 2021. doi.org/10.1021/bk-2021-1391
3. Worch, J.C.; Dove, A.P. 100th Anniversary of macromolecular science viewpoint: Toward catalytic chemical recycling of waste (and future) plastics. *ACS Macro Lett.* **2020**, *9*, 1494–1506. doi.org/10.1021/acsmacrolett.0c00582
4. Chu, M.; Liu, Y.; Lou, X.; Zhang, Q.; Chen, J. Rational design of chemical catalysis for plastic recycling. *ACS Catal*. **2022**, *12*, 4659–4679. doi.org/10.1021/acscatal.2c01286
5. Zhang, X.; Fevre, M.; Jones, G.O.; Waymouth, R.M. Catalysis as an enabling science for sustainable polymers. *Chem. Rev*. **2018**, *118*, 839–885. doi.org/10.1021/acs.chemrev.7b00329
6. Westhues, S.; Idel, J.; Klankermayer, J. Molecular catalyst systems as key enablers for tailored polyesters and polycarbonate recycling concepts. *Sci. Adv.* **2018**, *4*, eaat966. doi/10.1126/sciadv.aat9669

7. Basterretxea, A.; Jehanno, C.; Mecerreyes, D.; Sardon, H. Dual organocatalysts based on ionic mixtures of acids and bases: A step toward high temperature polymerizations. *ACS Macro Lett.* **2019**, *8*, 1055–1062. doi.org/10.1021/acsmacrolett.9b00481
8. Payne, J.; Jones, M.D. The chemical recycling of polyesters for a circular plastics economy: Challenges and emerging opportunities. *ChemSusChem*. **2021**, *14*, 4041–4070. doi.org/10.1002/cssc.202100400
9. Häußler, M.; Eck, M.; Rothauer, D.; Mecking, S. Closed-loop recycling of polyethylene-like materials. *Nature* **2021**, *590*, 423–427. doi.org/10.1038/s41586-020-03149-9
10. Allen, R.D.; James, M.I. Chemical Recycling of PET. In *Circular Economy of Polymers: Topics in Recycling Technologies*; Collias, D.I., James, M.I., Layman, J.M., Eds.; ACS Symposium Series; American Chemical Society: Washington, DC, USA, 2021; pp. 61–80.
11. Paszun, D.; Spychaj, T. Chemical recycling of poly(ethylene terephthalate). *Ind. Eng. Chem. Res*. **1997**, *36*, 1373–1383. doi.org/10.1021/ie960563c
12. Damayanti; Wu, H.S. Strategic possibility routes of recycled PET. *Polymers* **2021**, *13*, 1475. doi.org/10.3390/polym13091475
13. McNeeley, A.; Liu, Y. A. Assessment of PET depolymerization processes for circular economy. 1. Thermodynamics, chemistry, purification, and process design. *Ind. Eng. Chem. Res.* **2024**, *63*, 3355-3399. doi.org/10.1021/acs.iecr.3c04000
14. Jehanno, C.; Pérez-Madrigal, M. M.; Demarteau, J.; Sardon, H.; Dove, A. P. Organocatalysis for depolymerization. *Polym. Chem*. **2019**, *10*, 172-186. doi.org/10.1039/C8PY01284A
15. de Dios Caputto, M. D.; Navarro, R.; Valentín, J. L.; Marcos-Fernández, Á. Chemical upcycling of poly(ethylene terephthalate) waste: Moving to a circular model. *J. Polym. Sci*. **2022**, *60*, 3269-3283. doi.org/10.1002/pol.20220137
16. Dupont, L.A.; Gupta, V.P. Degradative transesterification of terephthalate polyesters to obtain DOTP plasticizer for flexible PVC. *J. Vinyl. Technol*. **1993**, *15*, 100–104. doi.org/10.1002/vnl.730150210
17. Chen, J.-W.; Chen, L.-W. The glycolysis of poly(ethylene terephthalate). *J. Appl. Polym. Sci.* **1999**, *73*, 35–40. doi.org/10.1002/(SICI)1097-4628(19990705)73:1<35::AID-APP4>3.0.CO;2-W
18. Chen, C.-H.; Chen, C.-Y.; Lo, Y.-W.; Mao, C.-F.; Liao, W.-T. Studies of glycolysis of poly(ethylene terephthalate) recycled from postconsumer soft-drink bottles. I. Influences of glycolysis conditions. *J. Appl. Polym. Sci*. **2001**, *80*, 943–948. doi.org/10.1002/app.1174
19. Mansour, S.H.; Ikladious, N.E. Depolymerization of poly(ethylene terephthalate) wastes using 1,4-butanediol and triethylene glycol. *Polym. Test*. **2002**, *21*, 497–505. doi.org/10.1016/S0142-9418(01)00115-5
20. Kurokawa, H.; Ohshima, M.; Sugiyama, K.; Miura, H. Methanolysis of polyethylene terephthalate (PET) in the presence of aluminium tiisopropoxide catalyst to form dimethyl terephthalate and ethylene glycol. *Polym. Degrad. Satbil*. **2003**, *79*, 529–533. doi.org/10.1016/S0141-3910(02)00370-1
21. Troev, K.; Grancharov, G.; Tsevi, R.; Gitsov, I. A novel catalyst for the glycolysis of poly (ethylene terephthalate). *J. Appl. Polym. Sci*. **2003**, *90*, 1148–1152. doi.org/10.1002/app.12711
22. López-Fonseca, R.; Duque-Ingunza, I.; de Rivas, B.; Arnaiz, S.; Gutiérrez-Ortiz, J.I. Chemical recycling of post-consumer PET wastes by glycolysis in the presence of metal salts. *Polym. Degrad. Stab*. **2010**, *95*, 1022–1028. doi.org/10.1016/j.polymdegradstab.2010.03.007
23. Fukushima, K.; Coulembier, O.; Lecuyer, J.M.; Almegren, H.A.; Alabdulrahman, A.M.; Alsewailem, F.D.; Mcneil, M.A.; Dubois, P.; Waymouth, R.M.; Horn, H.W.; et al. Organocatalytic depolymerization of poly(ethylene terephthalate). *J. Polym. Sci., Part A Polym. Chem.* **2011**, *49*, 1273–1281. doi.org/10.1002/pola.24551
24. Fukushima, K.; Coady, D.J.; Jones, G.O.; Almegren, H.A.; Alabdulrahman, A.M.; Alsewailem, F.D.; Horn, H.W.; Rice, J.E.; Hedrick, J.L. Unexpected efficiency of cyclic amidine catalysts in depolymerizing poly(ethylene terephthalate). *J. Polym. Sci. Part A Polym.Chem*. **2013**, *51*, 1606–1611. doi.org/10.1002/pola.26530
25. Imran, M.; Kim, D.H.; Al-Masry, W.A.; Mahmood, A.; Hassan, A.; Haider, S.; Ramay, S.M. Manganese-, cobalt-, and zinc-based mixed-oxide spinels as novel catalysts for the chemical recycling of poly(ethylene terephthalate) via glycolysis. *Polym. Degrad. Satbil*. **2013**, *98*, 904–915. doi.org/10.1016/j.polymdegradstab.2013.01.007

 doi:10.20944/preprints202501.0484.v1

26. Liu, S.W.; Wang, Z.P.; Li, L.; Yu, S.T.; Xie, C.X.; Liu, F.S. Butanol alcoholysis reaction of polyethylene terephthalate using acidic ionic liquid as catalyst. *J. Appl. Polym. Sci.* **2013**, *130*, 1840–1844. https://doi.org/10.1002/app.39246.
27. Liu, B.; Fu, W.; Lu, X.; Zhou, Q.; Zhang, S. Lewis acid–base synergistic catalysis for polyethylene terephthalate degradation by 1,3-Dimethylurea/Zn(OAc)$_2$ deep eutectic solvent. *ACS Sustain. Chem. Eng*. **2018**, *7*, 3292–3300. doi.org/10.1021/acssuschemeng.8b05324
28. Wang, Q.; Geng, Y.; Lu, X.; Zhang, S. First-row transition metal-containing ionic liquids as highly active catalysts for the glycolysis of poly(ethylene terephthalate) (PET). *ACS Sustai. Chem. Eng.* **2015**, *3*, 340-348. doi.org/10.1021/sc5007522
29. Liu, B.; Fu, W.; Lu, X.; Zhou, Q.; Zhang,;S. Lewis acid–base synergistic catalysis for polyethylene terephthalate degradation by 1,3-dimethylurea/Zn(OAc)$_2$ deep eutectic solvent, *ACS Sustain. Chem. Eng.* **2019**, *7*, 3292-3300. doi.org/10.1021/acssuschemeng.8b05324
30. Jehanno, C.; Demarteau, J.; Mantione, D.; Arno, M. C.; Ruipérez, F.; Hedrick, J. L.; Dove, A. P.; Sardon, H. Selective chemical upcycling of mixed plastics guided by a thermally stable organocatalyst. *Angew. Chem. Int. Ed.*, 2021, **60**, 6710-6717. doi.org/10.1002/anie.202014860
31. Kaiho, S.; Hmayed, A. A. R.; Chiaie, K. R. D.; Worch, J. C.; Dove, A.P. Designing thermally stable organocatalysts for poly(ethylene terephthalate) synthesis: Toward a one-pot, closed-loop chemical recycling system for PET. *Macromolecules* **2022**, *55*, 10628–10639. doi.org/10.1021/acs.macromol.2c01410
32. Chiaie, K. R. D.; McMahon, F. R.; Williams, E. J.; Price, M. J.; Dove, A. P. Dual-catalytic depolymerization of polyethylene terephthalate (PET). *Polym. Chem*. **2020**, *11*, 1450–1453. doi.org/10.1039/C9PY01920K
33. Rollo, M.; Raffi, F.; Rossi, E.; Tiecco, M.; Martinell, E.; Ciancaleoni, G. Depolymerization of polyethylene terephthalate (PET) under mild conditions by Lewis/Brønsted acidic deep eutectic solvents. *Chem. Eng. J*. **2023**, *456*, 141092. doi.org/10.1016/j.cej.2022.141092
34. de Dios Caputto, M. D.; Navarro, R.; Valentín, J. L.; Marcos-Fernandez, A. Tuning of molecular weight and chemical composition of polyols obtained from poly(ethylene terephthalate) waste recycling through the application of organocatalysts in an upcycling route. *J. Clean. Prod.* **2024**, *454*, 142253. doi.org/10.1016/j.jclepro.2024.142253
35. Du, J.-T.; Sun, Q.; Zeng, X.-F.; Wang, D.; Wang, J.-X.; Chen, J.-F. ZnO Nanodispersion as pseudohomogeneous catalyst for alcoholysis of polyethylene terephthalate. *Chem. Eng. Sci*. **2020**, *220*, 115642–115651. doi.org/10.1016/j.ces.2020.115642
36. Pham, D.D.; Cho, J. Low-energy catalytic methanolysis of poly(ethylene terephthalate). *Green Chem.* **2021**, *23*, 511–525. doi.org/10.1039/D0GC03536J
37. Shirazimoghaddam, S.; Amin, I.; Faria Albanese, J. A.; Shiju, N. R. Chemical recycling of used PET by glycolysis using niobia-based catalysts. *ACS Eng. Au*, **2023**, *3*, 37-44. doi.org/10.1021/acsengineeringau.2c00029
38. Tanaka, S.; Sato, J.; Nakajima, Y. Capturing ethylene glycol with dimethyl carbonate towards depolymerisation of polyethylene terephthalate at ambient temperature. *Green Chem*. **2021**, *23*, 9412–9416. doi.org/10.1039/D1GC02298A
39. Tanaka, S.; Koga, M.; Kuragano, T.; Ogawa, A.; Ogiwara, H.; Sato, K.; Nakajima, Y. Depolymerization of polyester fibers with dimethyl carbonate-aided methanolysis. *ACS Mater. Au* **2024**, *4*, 335–345. doi.org/10.1021/acsmaterialsau.3c00091
40. Abe, R.; Komine, N.; Nomura, K.; Hirano, M. La(iii)-Catalysed degradation of polyesters to monomers via transesterifications. *Chem. Commun*. **2022**, *58*, 8141–8144. doi.org/10.1039/D2CC02448A
41. Ohki, Y.; Ogiwara, Y.; Nomura, K. Depolymerization of polyesters by transesterification with ethanol using (cyclopentadienyl)titanium trichlorides. *Catalysts* **2023**, *13*, 421. doi.org/10.3390/catal13020421
42. Unruean, P.; Padungros, P.; Nomura, K., Kitiyanan, B. Efficient chemical depolymerization of polyethylene terephthalate via transesterification with ethanol using CaO catalyst. *J. Mater. Cycles Waste Manag.* **2024**, *26*, 731-740. doi.org/10.1007/s10163-023-01823-4
43. Peng, Y.; Yang, J.; Deng, C.; Deng, J.; Shen, L.; Fu, Y. Acetolysis of waste polyethylene terephthalate for upcycling and life-cycle assessment study, *Nat. Commun.* **2023**, *14*, 3249. doi.org/10.1038/s41467-023-38998-1

44. Nomura, K.; Aoki, T.; Ohki, Y.; Kikkawa, S.; Yamazoe, S. Transesterification of methyl-10-undecenoate and poly(ethylene adipate) catalyzed by (cyclopentadienyl)titanium trichlorides as model chemical conversions of plant oils and acid-, base-free chemical recycling of aliphatic polyesters. *ACS Sustain. Chem. Eng*. **2022**, *10*, 12504–12509. doi.org/10.1021/acssuschemeng.2c04877
45. Sudhakaran, S.; Siddiki, S.M.A.H.; Kitiyanan, B.; Nomura, K. CaO catalyzed transesterification of ethyl 10-undecenoate as a model reaction for efficient conversion of plant oils and their application to depolymerization of aliphatic polyesters. *ACS Sustain. Chem. Eng*. **2022**, *10*, 12864–12872. doi.org/10.1021/acssuschemeng.2c04287
46. Kobayashi, N.; Komine, N.; Nomura, K.; Hirano, H.; Hirano, M. La(III)-catalyzed depolymerization of poly(l-lactic acid) yielding chiral lactates. *Bull. Chem. Soc. Jpn.*, **2023**, *96*, 1324-1330. doi.org/10.1246/bcsj.20230183
47. Awang, N. W. B.; Hadiyono, M. A. B. R.; Abdellatif, M. M.; Nomura, K. Depolymerization of PET with ethanol by homogeneous iron catalysts applied for exclusive chemical recycling of cloth waste. *Ind. Chem Mat*. **2024**, web released on August 6. doi.org/10.1039/D4IM00081A
48. Ogiwara, Y.; Nomura, K. Chemical upcycling of PET into a morpholine amide as a versatile synthetic building block. *ACS Org. Inorg. Au* **2023**, *6*, 377-383. doi.org/10.1021/acsorginorgau.3c00037
49. Bepari, M. R.; Sullivan, L. R.; O'Harra, K. E.; Barbosa, G. D.; Turner, C. H.; Bara, J. E. Depolymerizing polyethylene terephthalate (PET) via "imidazolysis" for obtaining a diverse array of intermediates from plastic waste. *ACS Applied Polymer Materials* **2024**, *6*, 7886-7896. doi.org/10.1021/acsapm.4c01525