Supporting Information for

An Upcycling Strategy for Polyamide 6: Preparing Thermoplastic Polyamide Elastomers from Glycolysates Produced by Controlled Degradation

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1. Supplementary Figures and Tables

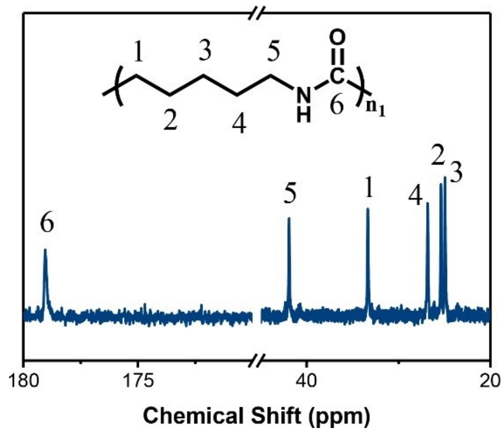


Fig. S1 ^{13}C NMR spectra of PA6-3h-5wt%.

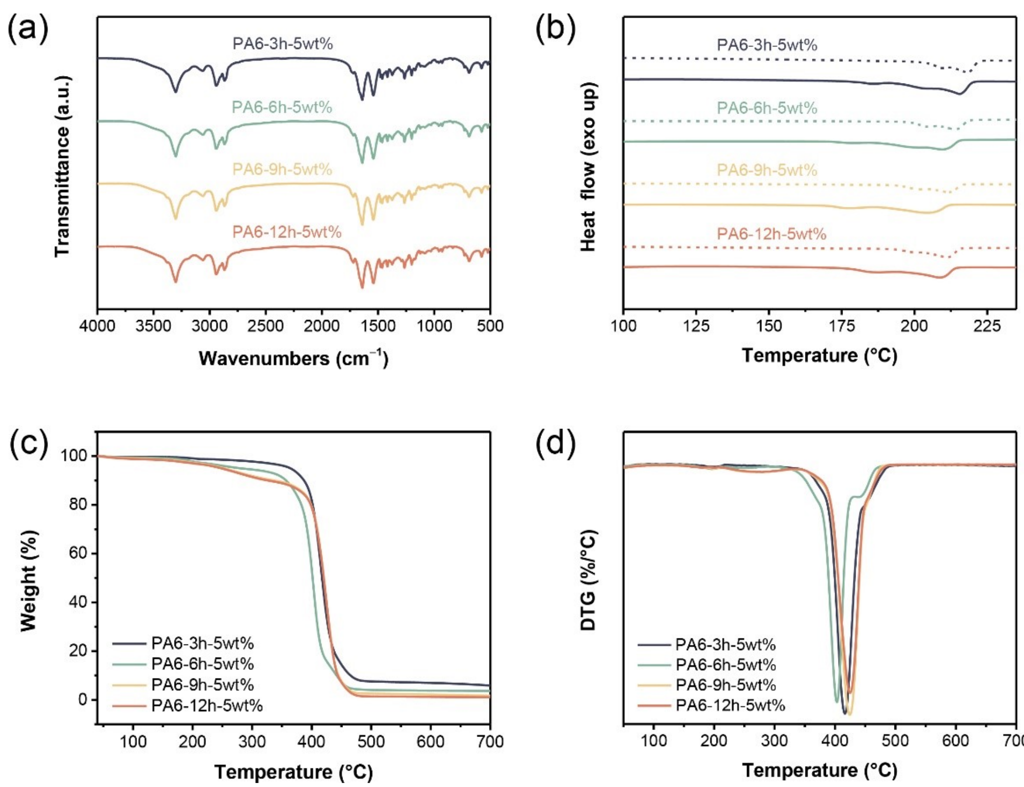
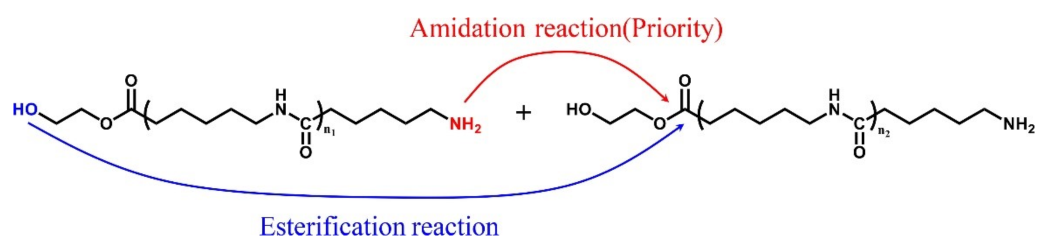


Fig. S2 (a) FTIR spectra of PA6-Xh-5wt%; (b) DSC curves of PA6-Xh-5wt% during the primary and secondary heating (Solid line is primary heating, dashed line is secondary heating); TG (c) and DTG (d) curves of PA6-Xh-5wt% in nitrogen atmosphere.

Table S1 Melting point and melting range parameters of the DSC curves of PA6-Xh-Ywt% for primary and secondary temperature rise.

Sample	Melting point of primary heating (°C)	Melting range of primary heating (°C)	Melting point of secondary heating (°C)	Melting range of secondary heating (°C)
PA6	224.0	209.3 ~ 227.6	221.6	210.5 ~ 226.3
PA6-3h-5wt%	215.4	195.8 ~ 220.8	218.2	203.7 ~ 222.6
PA6-3h-10wt%	215.3/188.3	183.4 ~ 219.1	217.9	202.9 ~ 221.8
PA6-3h-15wt%	211.0/190.8	182.7 ~ 217.3	217.4	199.9 ~ 221.2
PA6-3h-20wt%	211.1/190.2	182.5 ~ 216.4	215.9	196.5 ~ 220.5
PA6-6h-5wt%	209.9	188.8 ~ 215.9	214.3	198.2 ~ 218.6
PA6-9h-5wt%	208.9	178.1 ~ 214.4	212.2	194.1 ~ 216.7
PA6-12h-5wt%	205.1	169.5 ~ 212.4	211.6	190.9 ~ 216.2



Scheme S1 Schematic diagram of the mechanism of possible reactions between molecules of PA6 glycolysis oligomers.

Table S2 TG data of PA6-Xh-Ywt% in N_2.

Sample	$T_{5\%}$ (°C)	T_{max} (°C)
PA6	372.2	415.7
PA6-3h-5wt%	364.0	416.3
PA6-3h-10wt%	325.2	408.9
PA6-3h-15wt%	237.5	424.3
PA6-3h-20wt%	231.6	408.5
PA6-6h-5wt%	279.9	403.4
PA6-9h-5wt%	251.9	424.2
PA6-12h-5wt%	247.9	426.8

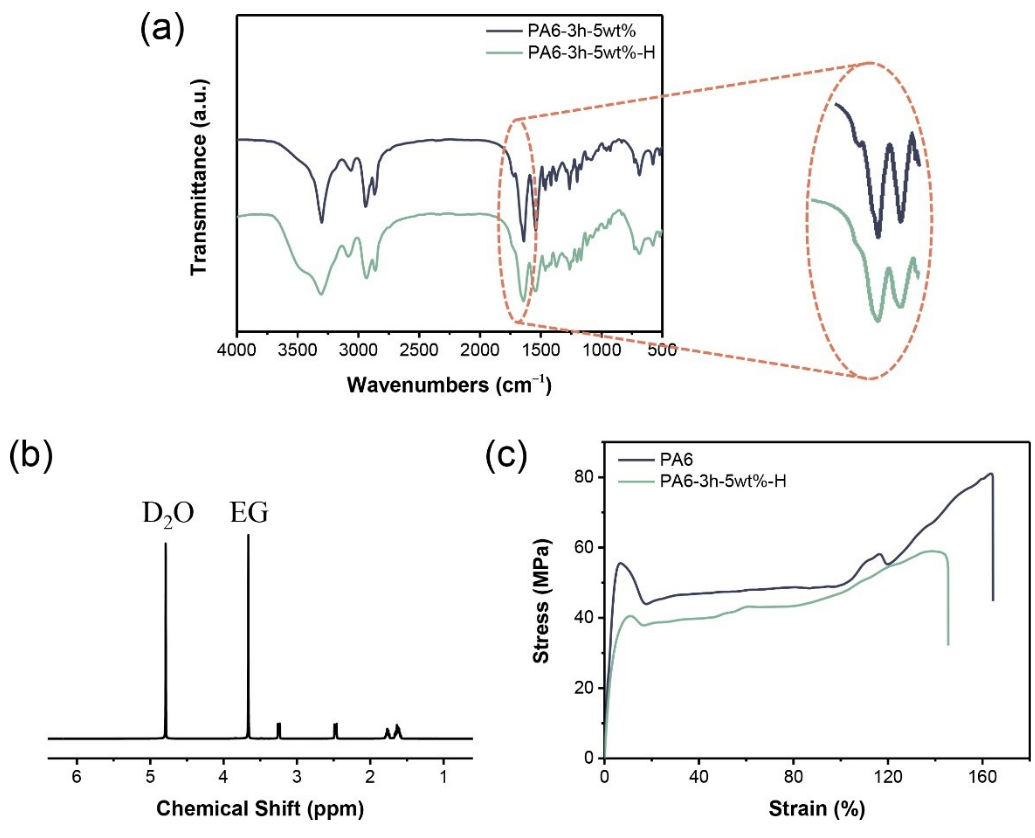


Fig. S3 (a) FTIR spectra of PA6-3h-5wt% and PA6-3h-5wt%-H; (b) ^{1}H NMR spectra of volatiles during heating of PA6-3h-5wt%; (c) The tensile stress-strain curves of PA6 and PA6-3h-5wt%-H.

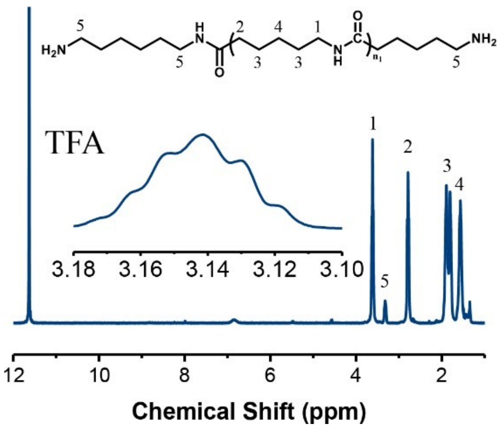


Fig. S4 ^{1}H NMR spectra of PA6-3h-5wt%-N.

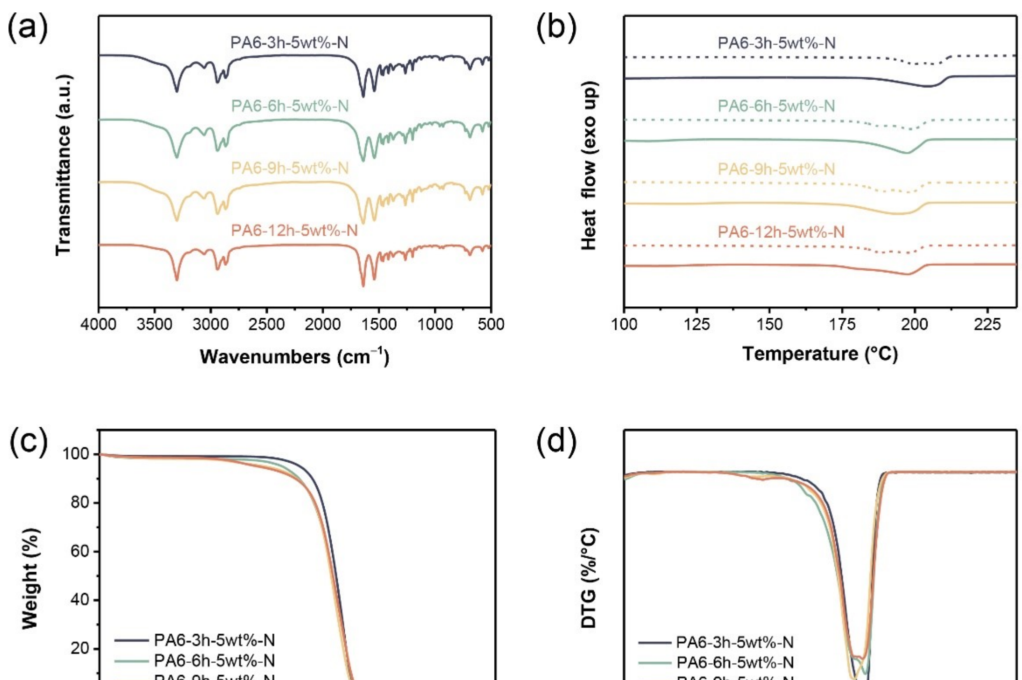


Fig. S5 (a) FTIR spectra of PA6-Xh-5wt%-N; (b) DSC curves of PA6-Xh-5wt%-N during the primary and secondary heating (Solid line is primary heating, dashed line is secondary heating); TG (c) and DTG (d) curves of PA6-Xh-5wt%-N in nitrogen atmosphere.

Table S3 The melting points of PA6-Xh-Ywt%-N. (Notes: T_{m1} and T_{m1} correspond to the DSC primary and secondary heating melting points of PA6-Xh-Ywt%-N respectively.)

Sample	T_{m1} (°C)	T_{m2} (°C)
PA6-3h-5wt%-N	205.9	206.6
PA6-3h-10wt%-N	201.6	201.8
PA6-3h-15wt%-N	195.0	195.8
PA6-3h-20wt%-N	190.3	191.7
PA6-6h-5wt%-N	197.6	199.1
PA6-9h-5wt%-N	195.2	198.3
PA6-12h-5wt%-N	197.8	197.6

Table S4 TG data of PA6-Xh-Ywt%-N in N_2.

Sample	$T_{5\%}$ (°C)	T_{max} (°C)
PA6-3h-5wt%-N	368.1	446.3
PA6-3h-10wt%-N	359.4	434.3
PA6-3h-15wt%-N	310.2	452.7
PA6-3h-20wt%-N	286.3	450.0
PA6-6h-5wt%-N	345.2	448.7
PA6-9h-5wt%-N	316.0	432.3
PA6-12h-5wt%-N	304.9	445.0

Table S5 M_n, M_η and GD of PA6-Xh-Ywt%-N.

Sample	M_η (g/mol)	M_n (g/mol)	GD (%)
PA6-3h-5wt%-N	2374 ± 41	1873 ± 55	23.4 ± 0.8
PA6-3h-10wt%-N	2278 ± 63	1679 ± 52	33.5 ± 0.6

PA6-3h-15wt%-N	2208 ± 35	1436 ± 42	40.0 ± 0.9
PA6-3h-20wt%-N	2120 ± 55	1344 ± 38	45.1 ± 1.2
PA6-6h-5wt%-N	2340 ± 42	1790 ± 45	32.8 ± 0.8
PA6-9h-5wt%-N	2270 ± 61	1675 ± 40	37.2 ± 1.0
PA6-12h-5wt%-N	2259 ± 54	1601 ± 35	40.5 ± 1.1

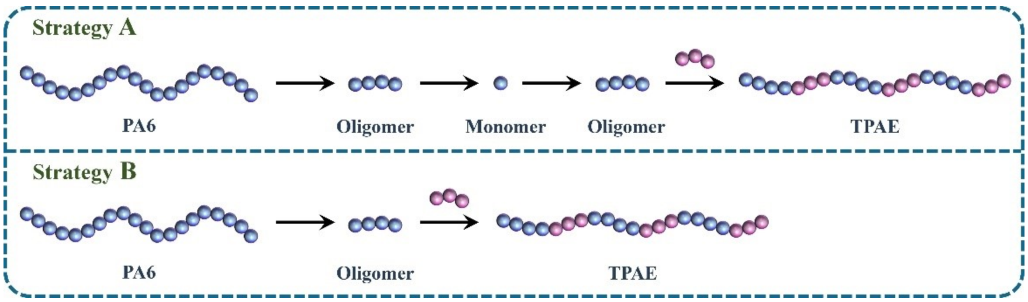
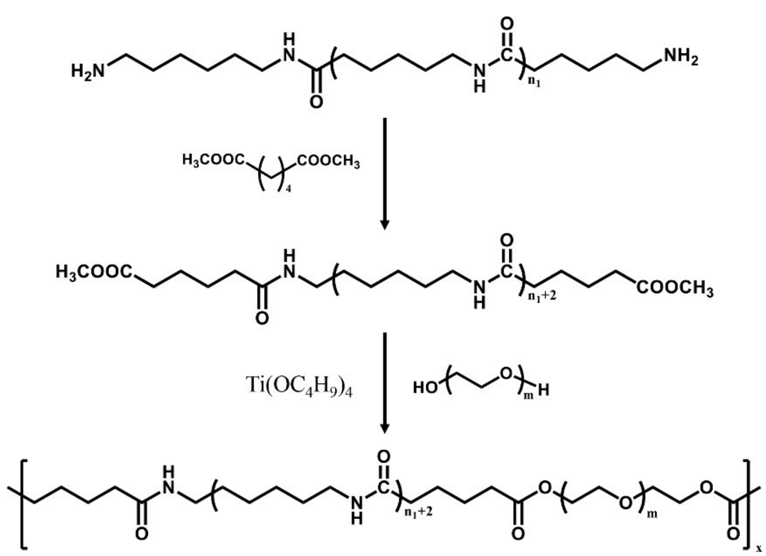


Fig. S6 The reaction routes to be followed for the preparation of TPAE by PA6 monomer (Strategy A) and oligomer (Strategy B) recycling methods.



Scheme S2 The synthesis route of TPAEs.

Table S6 Thermal parameters of TPAEs.(Notes: T_{mS} and ΔH_{mS} are thermal parameters of soft segment PEG, T_{mH} and ΔH_{mH} are thermal parameters of hard segment PA.)

Sample	T_{mS} (°C)	ΔH_{mS} (J/g)	T_{mH} (°C)	ΔH_{mH} (J/g)
T1	10.4	7.0	194.0	28.4
T2	9.6	5.7	192.3	28.9
T3	8.1	10.0	190.2	29.8
T4	7.9	9.4	189.1	27.9

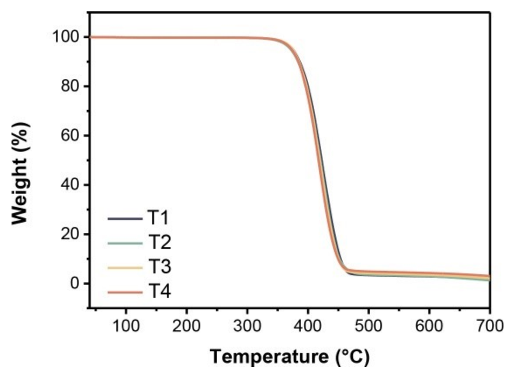


Fig. S7 TG curves of TPAEs.

Table S7 TG data of TPAEs in N_2.

Sample	$T_{5\%}$ (°C)	T_{max} (°C)
T1	374.9	424.3
T2	371.4	427.5
T3	374.7	420.5
T4	372.9	419.0

Table S8 Tensile data for TPAEs.

Sample	Young's modulus	Elongation at break	Fracture strength

	(MPa)	(%)	(MPa)
T1	210.7 ± 8.1	732 ± 67	40.9 ± 2.3
T2	176.1 ± 7.8	697 ± 50	36.2 ± 1.5
T3	138.2 ± 6.8	580 ± 73	28.7 ± 2.8
T4	116.5 ± 4.5	807 ± 54	35.6 ± 1.5

Table S9 Mechanical Properties Summary of TPAE Prepared by PA6.

Materials (Ref.)	Fracture strength (MPa)	Elongation at break (%)
PA6-PEG (This work)	28.7–40.9	580–807
PA6-PTMG (Ref. 31)	33−61	384−1220
PA6-PTMG (Ref. 32)	25–38	225–455
PA6-PEG (Ref. 34)	15.3–27.0	125–508
PA6-PEG (Ref. 35)	22.2–44.7	245–343
PA6-PTMG (Ref. 38)	29−63	93−514
PA6-PTMG (Ref. 39)	35.9	580
PA6-PTMG (Ref. 40)	About 32−55	About 670−1100

2. Techno-economic analysis (TEA)

2.1. Introduction to TEA

2.1.1. Analysis methods and indicators

TEA is a methodology used to evaluate technical projects, programs or decisions to determine their economic feasibility. In this study, the Annuity Techno Economic Assessment Method (ATEM)[1] is used to estimate the cost. The annualized capital investment cost ACC is calculated as follows, assuming that the annualized investment cost ACC is borrowed and repaid over the life of the plant at a specified loan rate.

$$ACC = FCI \times \frac{NIR \times (1+NIR)^N}{(1+NIR)^N - 1}$$

The total production cost is calculated as follows:

$$C_{total} = \frac{(ACC + CCOP)}{Annual\ Production}$$

2.1.2. Analytical Steps

In order to evaluate the economic feasibility of TPAE production from PA6 glycolysates, a TEA of the TPAE production process was carried out on the basis of test yields. The cost-benefit analysis included the following main steps:

(1) Define the objectives and scope of the project: Define the main objectives of the project and the scope to be covered. Clarifying the specific objectives of the project is critical to the direction and content of the subsequent analysis.

(2) Determination of costs and benefits: All costs associated with the project are collected, including investment costs (e.g., equipment purchase, construction costs, labor costs, etc.) and operational costs (e.g., maintenance costs, operation and management costs, etc.). At the same time, the life cycle costs of the project are considered, including the costs of the investment phase, the operation phase and the waste treatment phase. Finally, the expected economic benefits of the project are evaluated.

(3) Discounting costs and benefits to current values: Future costs and benefits are discounted to current values, taking into account the effect of time value. This is done to ensure that changes

in the time value of money are taken into account when comparing costs and benefits. Comparing costs and benefits: comparing the total costs of a project with the total benefits.

2.2. Definition of objective and scope

2.2.1. Introduction to the product manufacturing process

This study contains the fabrication of two products, the study case is the preparation of TPAE from the PA6 glycolysates in this work (T1). The comparison case is the preparation of TPAE (T1-CL) with exactly the same ratio of soft and hard segments as T1 by the one-pot method using CL monomer as the raw material.

Study case process description: Reaction route for the conversion of waste PA6 to thermoplastic polyamide elastomers. The reaction was carried out at 200 °C and atmospheric pressure with waste PA6, EG and H_3PO_4 for 3 h. The reaction was cooled and filtered, and the liquid portion, which consisted mainly of EG and H_3PO_4, was reused (the process included a 10 wt% loss), while the solid portion (PA6 oligomers) was washed and dried (the process included a 20 wt% loss of the PA6 oligomers). The PA6 oligomers were then reacted with HMDA, DMA, PEG_{1000}, and the catalyst $Ti(OC_4H_9)_4$ to obtain TPAE, respectively.The process was simplified to include a reaction at 220 °C for 3 h at atmospheric pressure, and a decompression for 3 h at 240 °C for 100 pa.

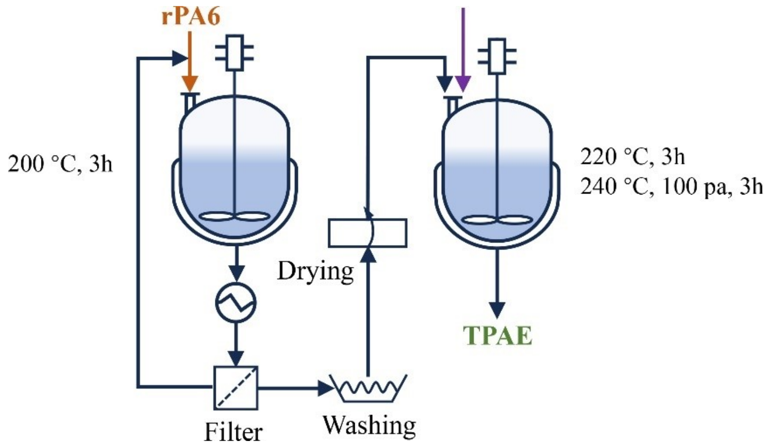


Fig. S8 Manufacturing Process of study case.

Comparison case process description: TPAE prepared by one-pot method, using water as the ring-opening agent to open the ring of caprolactam and adipic acid as the capping agent, the end-carboxylated PA6 oligomers were prepared first, and then the polyethylene glycol was added directly to react with the catalyst tetrabutyl titanate to obtain the TPAE. the process was simplified to 220 °C reaction for 7 h, and 240 °C decompression to 100 pa reaction for 3 h. The process was simplified by the use of a single-step process, which was carried out in the same way as that of the TPAE.

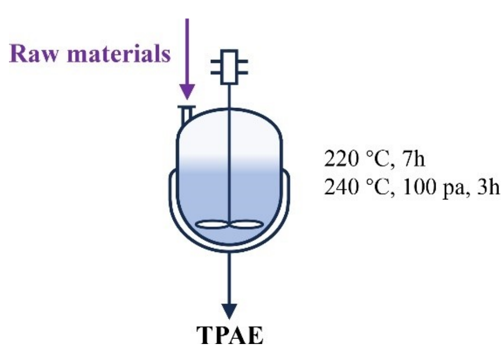


Fig. S9 Manufacturing Process of comparison case.

2.2.2. Basic assumptions for technical and economic evaluation

Table S10 Basic assumptions for TEA (Study Case).

Parameters	Value	Units	Ref
Annual operating hours	8000	h/y	
Plant life (N)	20	y	
NIR	10	%	
Scale (Annual production of TPAE)	1000000	t	
Scale (Yield of TPAE)	125	t/h	a
No. of equipment	100		
Mass flow rate to and from a single full mixing kettle	6.41	t/h	b
EG flow rate of single full mixing kettle	5.46	t/h	c
Feed ratio of PA6: EG: H_3PO_4	1: 6: 0.05		
Volume of a single full mixing kettle	25	m^3	
Volume of a single intermittent stirred-tank kettle	10	m^3	
Discount rate of EG and H_3PO_4	10	%	
Recycled PA6	400	\$/t	[2]
EG	621	\$/t	[3]
H_3PO_4	1315	\$/t	[4]
HMDA	2279	\$/t	[5]
DMA	1616	\$/t	[6]
$Ti(OC_4H_9)_4$	3176	\$/t	[7]
PEG_{1000}	1120	\$/t	[8]
Electricity price	0.042	\$/kwh	[9]
Area of a single heat exchanger	13.644	m^2	Aspen simulations yielded
Reference reactor power	23	kw	
Reference reactor volume	10	m^3	
Lang factor	3.63		[10]

a: Yield of TPAE (t/h) = Annual output of TPAE (1000000 t)/Annual operating hours (8000 h) = 125 t/h

b: Mass flow rate to and from a single full mixing kettle (t/h) = Logistics rPA6 flow rate (90.96 t/h)*(1+6+0.05)/No. of equipment (100) = 6.41 t/h

The rPA6 flow rates are detailed in Table S18.

c: EG flow rate of single full mixing kettle(t/h) = Logistics rPA6 flow rate (90.96 t/h)*6/No. of equipment (100)=5.46 t/h

Table S11 Basic assumptions for TEA (Comparison case).

Parameters	Value	Units	ref
Annual operating hours	8000	h/y	
Plant life(N)	20	y	
NIR	10	%	
Scale (Annual production of TPAE)	1000000	t	
Scale (Yield of TPAE)	125	t/h	a
No. of equipment	100		
Volume of a single intermittent stirred-tank kettle	15	m^3	
AA	1385	$/t	[11]
$Ti(OC_4H_9)_4$	3176	$/t	[7]
PEG_{1000}	1120	$/t	[8]
CL	1895	$/t	[12]
Electricity price	0.042	$/kwh	[9]
Reference reactor power	23	kw	
Reference reactor volume	10	m^3	
Lang factor	3.63		[10]

a: Yield of TPAE (t/h) = Annual output of TPAE (1000000 t)/Annual operating hours (8000 h) = 125 t/h

2.3. Cost

The system cost mainly includes investment cost and operation cost, the investment cost includes equipment purchase, construction cost and contingency cost, etc., the operation cost includes labor cost, maintenance cost, material and utility cost and management cost, etc., the cost analysis in this paper refers to the literature framework.[13, 14] The life cycle cost of the project is considered, including the cost of the investment phase and the operation phase.

2.3.1. Capital cost

Table S12 Calculation and reference of system capital cost (Study Case).

CAPITAL COSTS	Value	Units	Ref
ISBL	105756307	$	Table S13
OSBL	42302523	$	40%of ISBL
Engineering and construction costs	14805883	$	10% of ISBL+OSBL
Contingency charges	14805883	$	10% of ISBL+OSBL
Fixed Capital Investment (FCI)	177670595	$	Sum above

Table S13 Equipment cost (Study Case).

Equipment	Unit value	Units	Value	Units	Ref
Full mixing kettle	291692	$	29169167	$	a
Intermittent stirred-tank kettle	207819	$	20781946	$	a
Heat exchanger	23310	$	2330999	$	a
Filtrator	5960	$	596041	$	a (1 t = 2204.6 lb)
Install			191947697	$	=Lang factor* (Reaction kettle + Heat exchanger + Filtrator)[10]
Total plant ISBL			29169167	$	Sum above

a: The parameters related to the reference equipment are shown in Table S14, other parameters are shown in Table S10, and the equipment costing formula is as follows[15]:

$$Equipment\ cost = ref\ cost * \left(\frac{scale}{ref\ capacity}\right)^{scaling\ factor}$$

Total equipment price ($) = The price of a single device ($)*No. of equipment (100)

Table S14 Equipment parameters (Study Case).

Equipment	Reaction kettle[10]	Heat exchanger[16]	Filtrator[17]
Ref cost ($)	68597	20908	2795
Ref scale	0.5 m^3	10 m^2	8000 lb/h
Scaling factor	0.37	0.35	1.33

Table S15 Calculation and reference of system capital cost (Comparison case).

CAPITAL COSTS	Value	Units	REF
ISBL	111794639	$	Table S16
OSBL	44717856	$	40% of ISBL
Engineering and construction costs	15651249	$	10% of ISBL+OSBL
Contingency charges	15651249	$	10% of ISBL+OSBL
Fixed Capital Investment (FCI)	187814994	$	Sum above

Table S16 Equipment cost (Comparison case).

Equipment	Unit value	Unit	Value	Units	Ref
Intermittent stirred-tank kettle	241457	$	24145710	$	a
Install			87648929	$	=Lang factor*(Reaction kettle)[10]
Total plant ISBL			111794639	$	Sum above

a: The parameters related to the reference equipment are shown in Table S17 other parameters are shown in Table S11, and the equipment costing formula is as follows[15]:

$$Equipment\ cost\ =\ ref\ cost * \left(\frac{scale}{ref\ capacity}\right)^{scaling\ factor}$$

Table S17 Equipment parameters (Comparison Case).

Equipment	Ref cost ($)	Ref scale	Scaling factor
Reaction kettle[10]	68597	0.5 m^3	0.37

2.3.2. Operating cost

Table S18 Logistics data (Study Case).

□	Parameters	Value	Units	Value	Units	Note
Input	rPA6	100	t	90.96	t/h	a
	EG	6	t	5.46	t/h	10% loss rate
	H_3PO_4	0.05	t	0.0455	t/h	10% loss rate
	HMDA	5.54	t	5.04	t/h	110% theoretical addition
	DMA	16.8	t	15.28	t/h	110% theoretical addition

	PEG_{1000}	43.98	t	40.01	t/h
	$Ti(OC_4H_9)_4$	1.388	t	1.26	t/h
Output	TPAE	137.42	t	125	t/h

The mass flow rate (t/h) of rPA6 is converted according to the ratio, i.e:

The mass flow rate (t/h) of rPA6 = 100 t/137.42 t*125 t/h

Other substances as above.

Table S19 Energy flow data (Study Case).

	Parameters	Value	Units	Ref
Input	Power consumption (Full mixing kettle)	5750	kw	a
	Power consumption (Intermittent stirred-tank kettle)	2300	kw	b

a: Power consumption (Full mixing kettle) = Reference power (23 kw)*The volume of full mixing kettle (25 m^3)/The volume of reference kettle (10 m^3)*No. of equipment (100).

b: Power consumption (Intermittent stirred-tank kettle) = Reference power (23 kw)*The volume of intermittent stirred-tank kettle (10 m^3)/The volume of reference kettle (10 m^3)*No. of equipment (100).

Table S20 Logistics data (Comparison Case).

	Parameters	Value	Units	Value	Units	Note
Input	CL	7.9	t	79	t/h	a
	AA	0.58	t	5.8	t/h	
	PEG_{1000}	4	t	40	t/h	
	$Ti(OC_4H_9)_4$	0.13	t	1.3	t/h	
Output	TPAE	12.5	t	125	t/h	

The mass flow rate (t/h) of CL is converted according to the ratio, i.e:

The mass flow rate (t/h) of CL = 7.9 t/12.5 t*125 t/h

Other substances as above.

Table S21 Energy flow data (Comparison Case).

Parameters		Value	Units	Ref
Input	Power consumption (Intermittent stirred-tank kettle)	3450	kw	a

a: Power consumption (Intermittent stirred-tank kettle) = Reference power (23 kw)*The volume of intermittent stirred-tank kettle (15 m^3)/The volume of reference kettle (10 m^3)*No. of equipment (100).

2.3.3. Total cost of production

Table S22 Cost summary (Study Case).

Parameters	$/y	$/t TPAE
Fixed capital investment(FCI)	48312016	48
Fixed costs of production(FCOP)	17165888	17
Total Utilities (UTS)	270480000	270
rPA6	291078446	291
EG	27113957	27
H_3PO_4	478460	0.5
HMDA	92055135	92
DMA	197560763	198
PEG_{1000}	358445641	358
$Ti(OC_4H_9)_4$	32078940	32
Total Cost of Production	1334769246	1334

Table S23 Cost summary (Comparison Case).

Parameters	$/y	$/t TPAE
Fixed capital investment	22060679	22
Fixed costs of production(FCOP)	9250531	9
Total Utilities (UTS)	115920000	116
CL	1202188000	1202
AA	64264000	64
PEG_{1000}	358400000	358
$Ti(OC_4H_9)_4$	33030400	33
Total Cost of Production	1805113610	1805

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