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Supplementary Material

Assessing the conversion of various nylon polymers in the hydrothermal liquefaction of macroalgae

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1. Feedstock elemental compositions

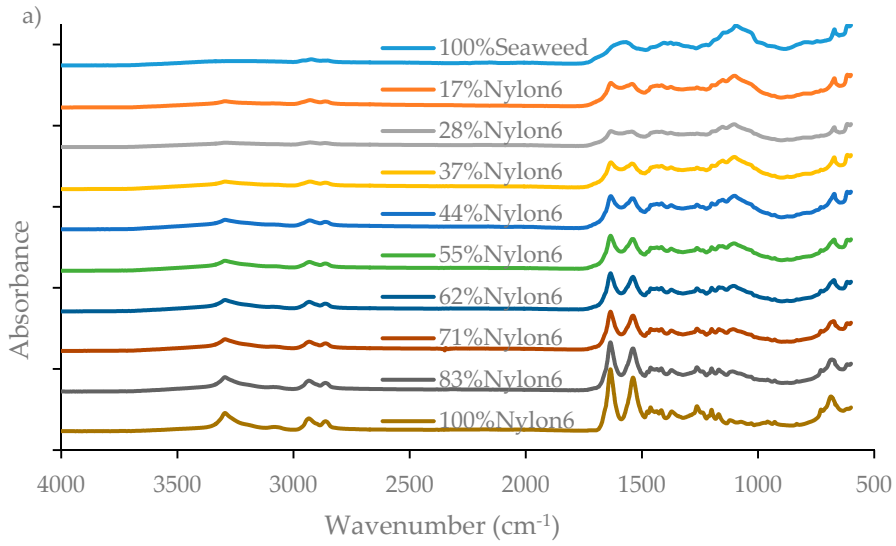
Table S1. Feedstock elemental compositions

Analysis	Seaweed	Nylon6	Nylon6/6	Nylon6/12	Nylon12
Moisture	4.9	-	-	-	-
Ash	25%	-	-	-	-
		Element Analysis (%)			
C	35.3	63.3	62.7	68.9	72.6
H	5.1	10.1	10.2	11.6	12.0
N	7.1	12.3	12.4	9.0	7.0
other	57.5	14.25	14.6	10.4	8.3
HHV	8.9	33.2	33.2	38.0	40.2
Component analysis (wt.%)					
Carbohydrate	53.6				
Protein	13.8				
Lipid	7.5				

2. Calibration curves for quantification of unreacted plastics in bio-char using FTIR

The conversion of nylons6 was estimated by plotting calibration curves of known amounts of the nylons with solid residue generated from the HTL reaction which contained only macroalgae biomass. Calibration curves were created for each nylon/biomass combination (nylon6/macroalgae, nylon66/macroalgae, nylon6,12/macroalgae, nylon 12/ macroalgae) by mixing bio-char from HTL of pure marine macroalgae with nylons at a range of known concentrations.

2.1 Nylon 6 in solid bio-char



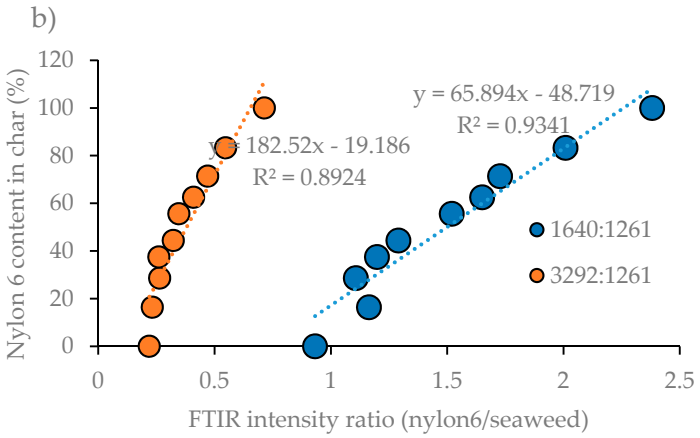
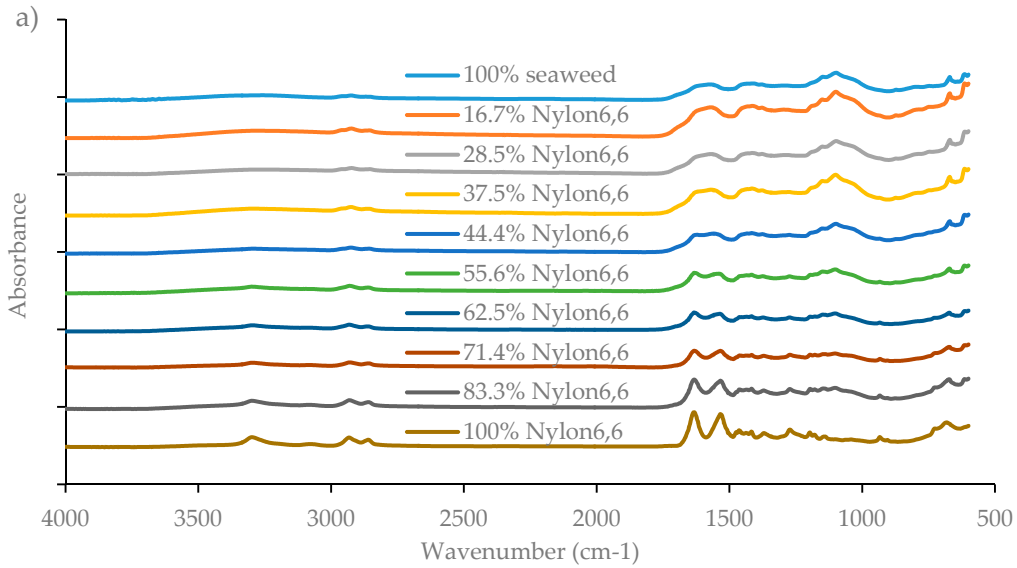


Figure S1. (a) FTIR spectra of macroalgae bio-char with different nylon6 contents, and (b) peak intensity ratio calibration curve for nylon6/6 content in macroalgae bio-char.

Table S2. Calculated percentage concentrations of unreacted nylon6 in bio-char from co-liquefaction of macroalgae with nylon6.

	Nylon 6	**Macroalgae solid residue**	**PIR**	**Predictive equation**	**R2**	**Estimated Nylon 6 content of char (%)**
	1640 cm^{-1}	**1261 cm^{-1}**	**1640:1261**	Y = 65.859x-48.934	0.94	
5% Nylon 6	0.01962	0.02332	0.84126			6.5 %
20% Nylon 6	0.03596	0.04031	0.8921			9.8%
50% Nylon 6	0.02047	0.01571	1.3031			36.8%
	3292 cm^{-1}	**1261 cm^{-1}**	**3292:1261**	Y= 199.82x – 17.088		
5 % Nylon 6	0.00114	0.02332	0.04895			0.0%
20 % Nylon 6	0.00561	0.04031	0.13906			6.0%
50 % Nylon 6	0.00894	0.01571	0.56932			84.4%

2.2 Nylon 6/6 in solid char



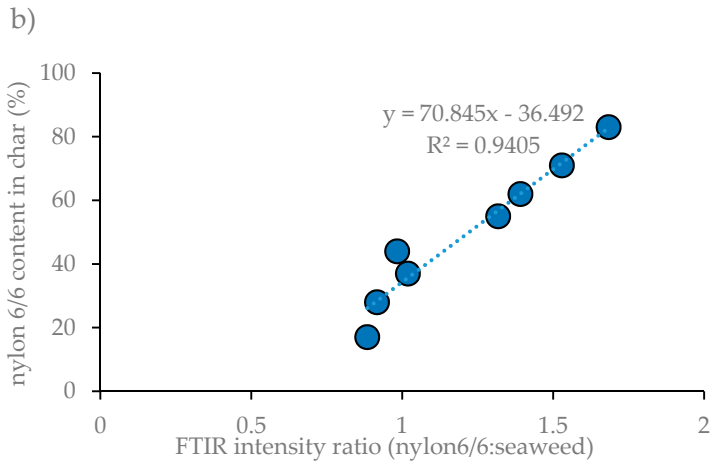
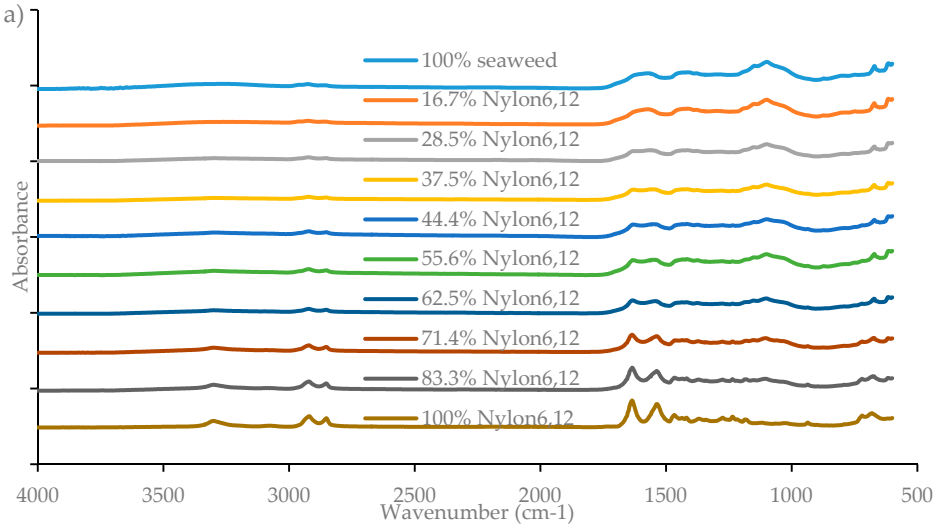


Figure S2. (a) FTIR spectra of macroalgae bio-char with different nylon6/6 contents, and (b) peak intensity ratio calibration curve for nylon6/6 content in macroalgae bio-char.

Table S3. Calculated percentage concentrations of unreacted nylon6/6 in bio-char from co-liquefaction of macroalgae with nylon6/6.

	Nylon 6/6	**seaweed solid residue**	**PIR**	**Predictive equation**	**R2**	**Estimated Nylon 6/6 content of char (%)**
	1640 cm^{-1}	**1261 cm^{-1}**	**1640:1261**	Y = 70.845x-36.492	0.94	
5% Nylon 6/6	0.02251	0.037211	0.604955			6.4 %
20% Nylon 6/6	0.03188	0.027787	1.147120			44.8%
50% Nylon 6/6	0.04821	0.03052	1.588451			76.0%

2.3 Nylon 6/12 in solid bio-char



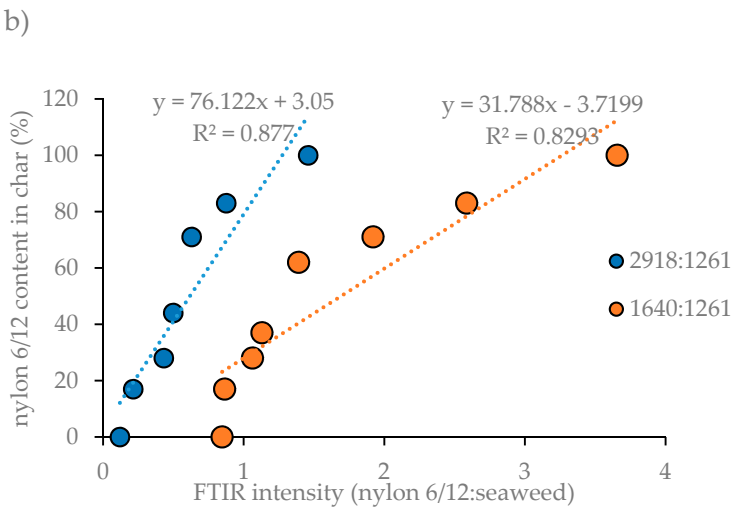


Figure S3. (a) FTIR spectra of macroalga io-char with different nylon6/12 contents, and (b) peak intensity ratio calibration curve for nylon6/12 content in macroalgae bio-char.

Table S4. Calculated percentage concentrations of unreacted nylon6/12 in bio-char from co-liquefaction of macroalgae with nylon6/12.

	Nylon 6/12	**seaweed solid residue**	**PIR**	**Predictive equation**	**R2**	**Estimated Nylon 6/12 content of char (%)**
	1640 cm^{-1}	1261 cm^{-1}	1640:1261	Y = 31.788-3.7199	0.83	
5% Nylon6/12	0.033626	0.036728	0.9155473			25.4 %
20% Nylon6/12	0.03394	0.022046	1.5396717			45.2%
50% Nylon6/12	0.05401	0.021718	2.4885014			75.4%
	2981 cm^{-1}	1261 cm^{-1}	2981:1261	Y= 76.122x + 3.05	0.88	
5 % Nylon 6/12	0.01232	0.036728	0.33532			28.6%
20 % Nylon 6/12	0.01865	0.022046	0.84611			67.5%
50 %Nylon 6/12	0.03917	0.02171	1.80478			140.4%

2.4 *Nylon 12 in solid bio-char*

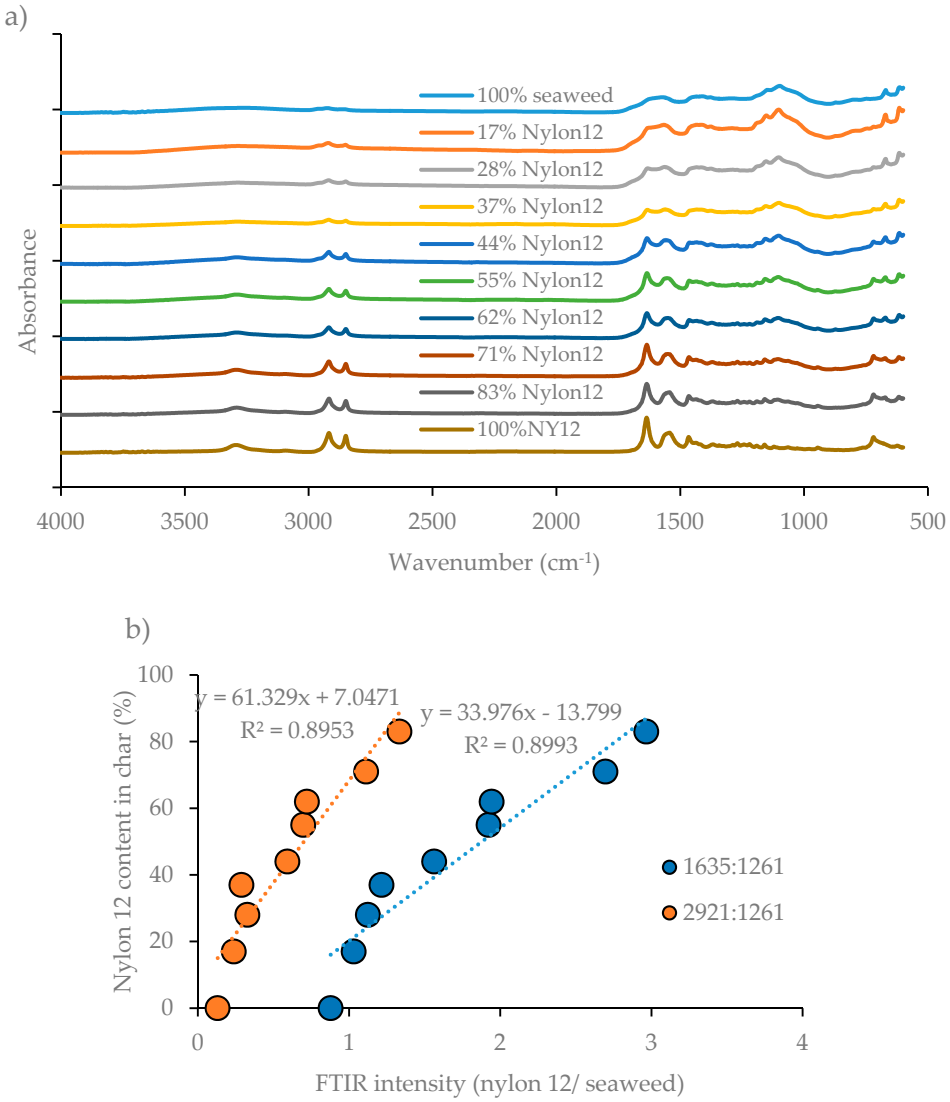


Figure S4. (a) FTIR spectra of macroalgae bio-char with different nylon12 contents, and (b) peak intensity ratio calibration curve for nylon12 content in macroalgae bio-char.

Table S5. Calculated percentage concentrations of unreacted nylon12 in bio-char from co-liquefaction of macroalgae with nylon12.

	Nylon 12	**Macroalgae solid residue**	**PIR**	**Predictive equation**	**R2**	**Estimated Nylon 6 content of char (%)**
	1635 cm^{-1}	1261 cm^{-1}	1635:1261	Y = 33.976x-13.799	0.8993	
5% Nylon 12	0.04848	0.04414	1.09848			23.0 %
20% Nylon 12	0.03356	0.01629	2.06066			56.2 %
50% Nylon 12	0.07234	0.02729	2.65072			76.3 %
	2912 cm^{-1}	1261 cm^{-1}	2912:1261	Y= 61.329x + 7.0471	0.8953	
5% Nylon 12	0.00617	0.04414	0.13984			32.9 %
20% Nylon 12	0.00297	0.01629	0.18255			40.6 %
50% Nylon 12	0.00143	0.02729	0.52393			102.6 %

3 Quantification of plastic conversion

$$Plastic\ in\ solid\ residue\ (g) = \frac{unconverted\ \ in\ solid\ residue\ (\%) \times\ solid\ residue\ yield\ (g)}{100}$$

$$Plastic\ convert\ (g) = plastic\ in\ feedstock - plastic\ in\ solid\ residue$$

$$Conversion\ (\%) = \frac{plastic\ convert\ (g) \times\ 100}{plastic\ in\ feedstock\ (g)}$$

Table S6. Summary of plastics conversion

Plastic components	Initial nylon in feedstock (g)	Total solid residue from reaction (g)	Estimated nylon content of char (%)	Amount of nylon in solid residue (g)	nylon conversion (%)
5% Nylon 6	0.15 g	0.98 g	0%	0.15 g	100%
20% Nylon 6	0.6 g	0.93 g	7.9%	0.53 g	88%
50% Nylon 6	1.50 g	0.93 g	61 %	0.94 g	62%
5% Nylon 6/6	0.15 g	1.07 g	6.4 %	0.08 g	54%
20% Nylon 6/6	0.6 g	1.09 g	44.8%	0.11 g	19%
50% Nylon 6/6	1.50 g	1.22 g	76%	0.57 g	38%
5% Nylon 6/12	0.15 g	1.09 g	25.4%	0 g	0%
20% Nylon 6/12	0.6 g	1.07 g	56%	0 g	0%
50% Nylon 6/12	1.50 g	1.66 g	108%	0 g	0%
5% Nylon 12	0.15 g	1.22 g	28.2 %	0 g	0%
20% Nylon 12	0.6 g	1.12 g	48.3%	0.06 g	9%
50% Nylon 12	1.50 g	1.50 g	89.4%	0.17 g	12%
5% Nylon line	0.15 g	0.66	6.2	0.041	73%
20% Nylon line	0.6 g	0.97	10.5	0.10	83%
50% Nylon line	1.50 g	1.10	62.4	0.69	54%

4. GC/MS analysis of bio-crudes

The identities of notable compounds in bio-crudes from co-liquefaction of macroalgal biomass with nylon blends, identified using GC/MS, are presented in Table S7 below.

Table S7. Identities of notable compounds in bio-crude products from co-liquefaction of macroalgal biomass with 20 wt.% nylons.

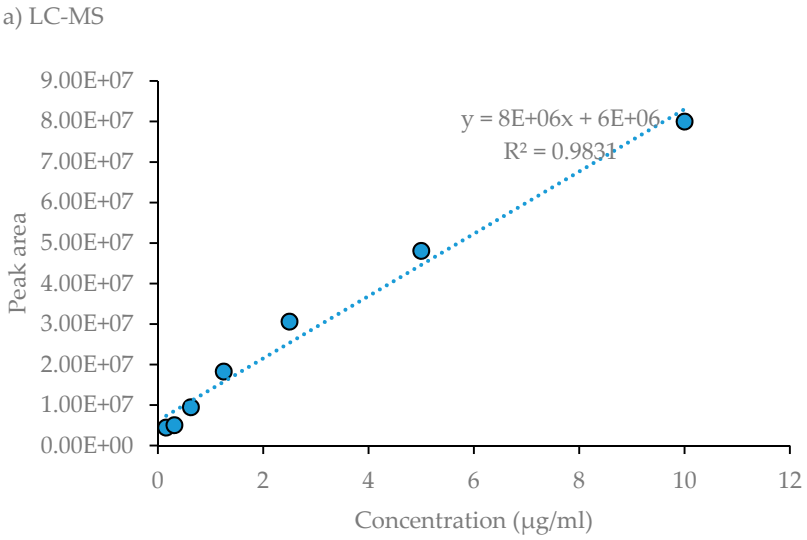
Compound identified	100% SW	20 wt.% NY6	20 wt.% NY6/6	20 wt.% NY6/12	20 wt.% NY12
Ethane, 1,1-diethoxy-	-			-	-
Toluene	-	-		-	
Formic acid, TBDMS derivative	-	-			-
Cyclopentanone	-			-	-
Butanoic acid					
Piperidine, 1-ethyl-					
1-Methoxy-2-propyl acetate	-			-	-
4-Piperidone	-	-		-	-
Hexamethylenimine	-	-			-
1-Butanamine, N-methyl-N-2-propenyl-	-	-	-		-
2-Cyclopenten-1-one, 2-methyl-					
Acetic acid, TBDMS derivative	-	-			-
Butyrolactone	-				
2-Cyclopenten-1-one, 3-methyl-					
Phenol					
2-Cyclopenten-1-one, 3,4-dimethyl-					
2-Cyclopenten-1-one, 2,3-dimethyl-					
Propanoic acid, TBDMS derivative	-	-			
Butyric Acid, TBDMS derivative					-

Compound identified	100% SW	20 wt.% NY6	20 wt.% NY6/6	20 wt.% NY6/12	20 wt.% NY12
p-Cresol					
tert-Butyldimethylsilyl methacrylate	-	-			-
Furan, 2-propyl-	-		-		-
2,5-Pyrrolidinedione, 1-methyl-					
Phenol, 2-methyl-					
Ethanone, 1-(1-cyclohexen-1-yl)-					
Ethanone, 1-(2-thienyl)-					
Phenylethyl Alcohol					
3-Pyridinol					
Caprolactam				-	-
m-Aminophenylacetylene	-	-			-
Phenol, p-tert-butyl-			-		-
Indole					
Dodecanamide			-		-
Tetradecanoic acid			-		
n-Hexadecanoic acid			-		-
Pentanoic acid	-	-			
Cyclododecanone	-	-	-		
Benzenesulfonamide, N-butyl-					-
9-Octadecenamide, (Z)-	-		-		-
Ethanol, 2-ethoxy-		-			-
Phthalic acid, cyclobutyl tridecyl ester	-		-	-	-
1,8-Diazacyclotetradecane-2,7-dione	-	-		-	-
Myristic acid, TBDMS derivative	-	-	-		

Compound identified	100% SW	20 wt.% NY6	20 wt.% NY6/6	20 wt.% NY6/12	20 wt.% NY12
Heneicosane	-	-	-		
Heptadecane	-	-	-		
Oleic Acid, (E)-, TBDMS derivative	-	-	-		-
Phthalic acid, di(2-propylpentyl) ester	-	-			

5. Yield of nylon product

The yield of nylon products from the system in both observed from aqueous and biocrude product from co-liquefaction of macroalgal biomass with nylon blends were estimated using LC/MS and GC/MS.



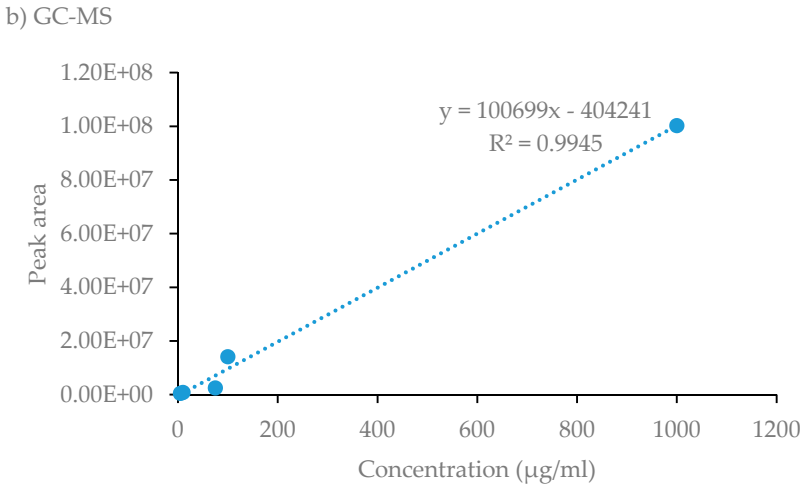


Figure S5. Calibration curve the peak area of ε-caprolactam by a) LC-MS, and b) GC-MS using the standard additional method

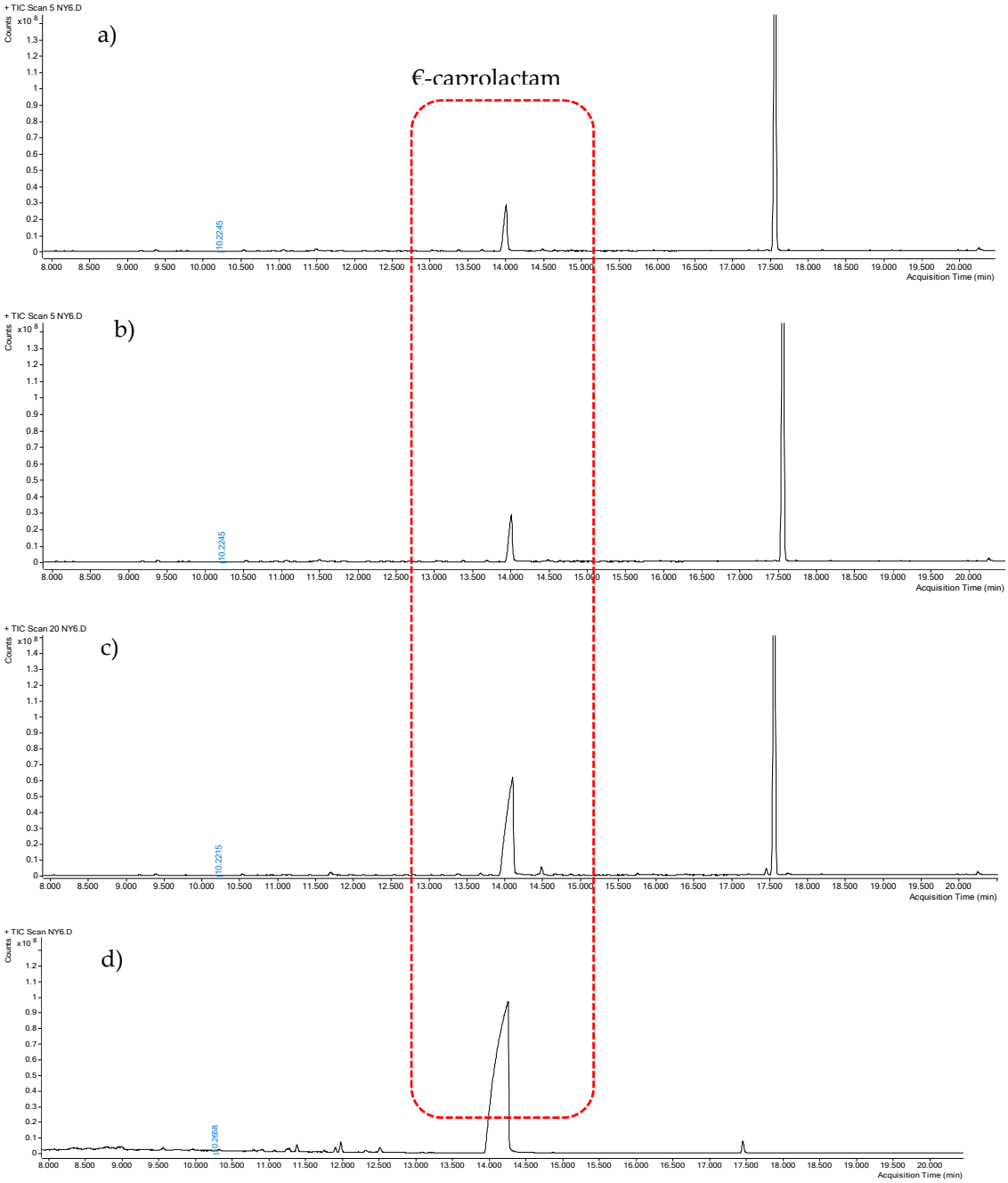


Figure S6. GC-MS chromatographs of bio-crude created from (a) 100%pure marine macroalgae, (b) 5 wt.% nylon 6 blend (c) 20 wt.% nylon 6 blend, and (d), 100 wt.% nylon 6