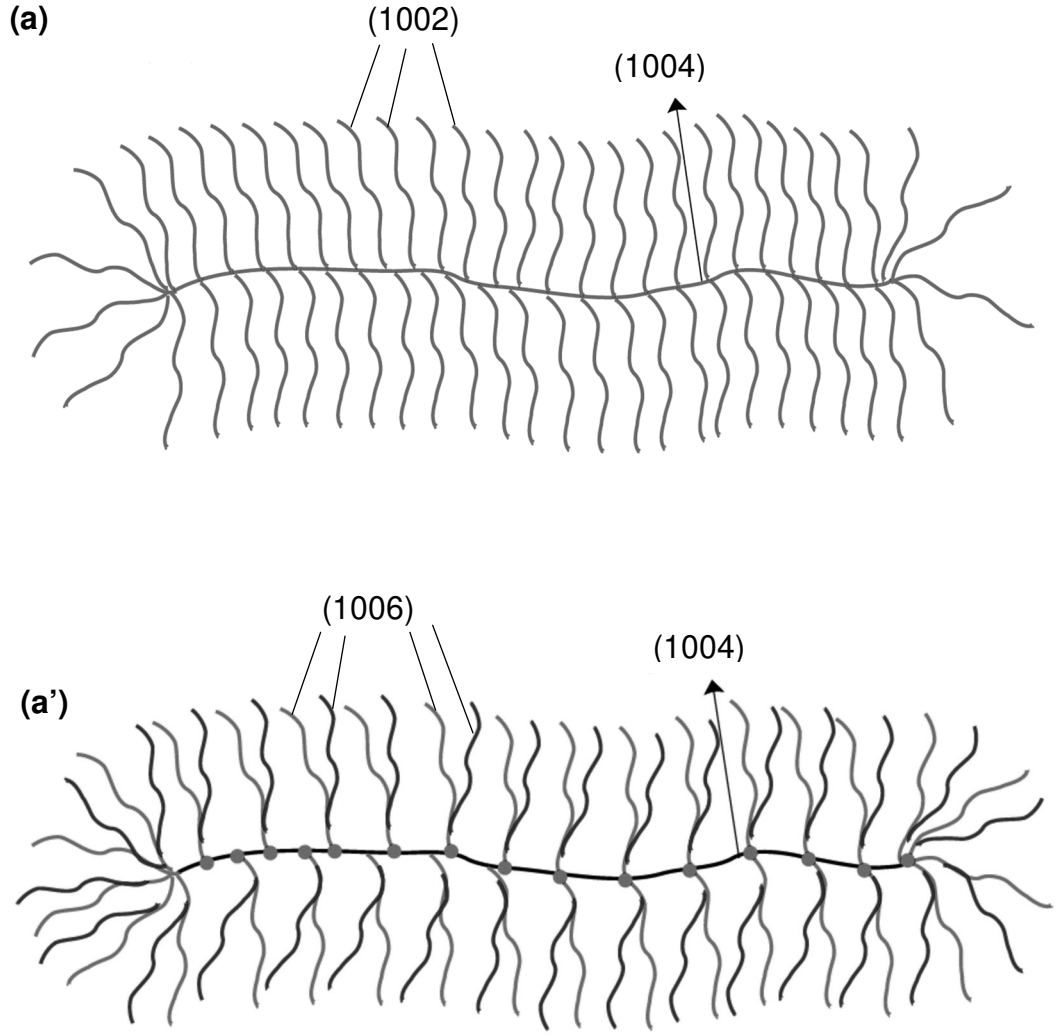
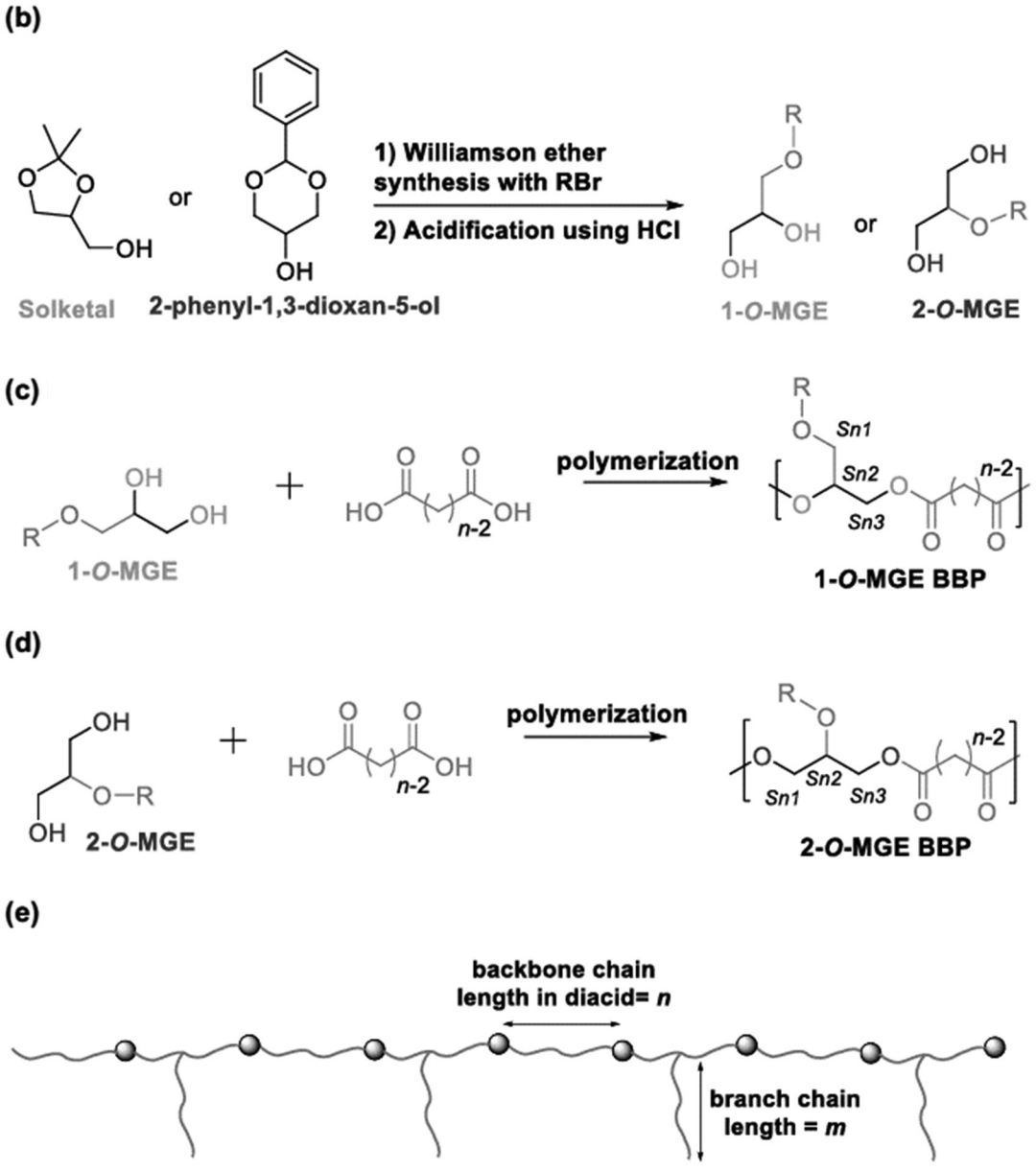
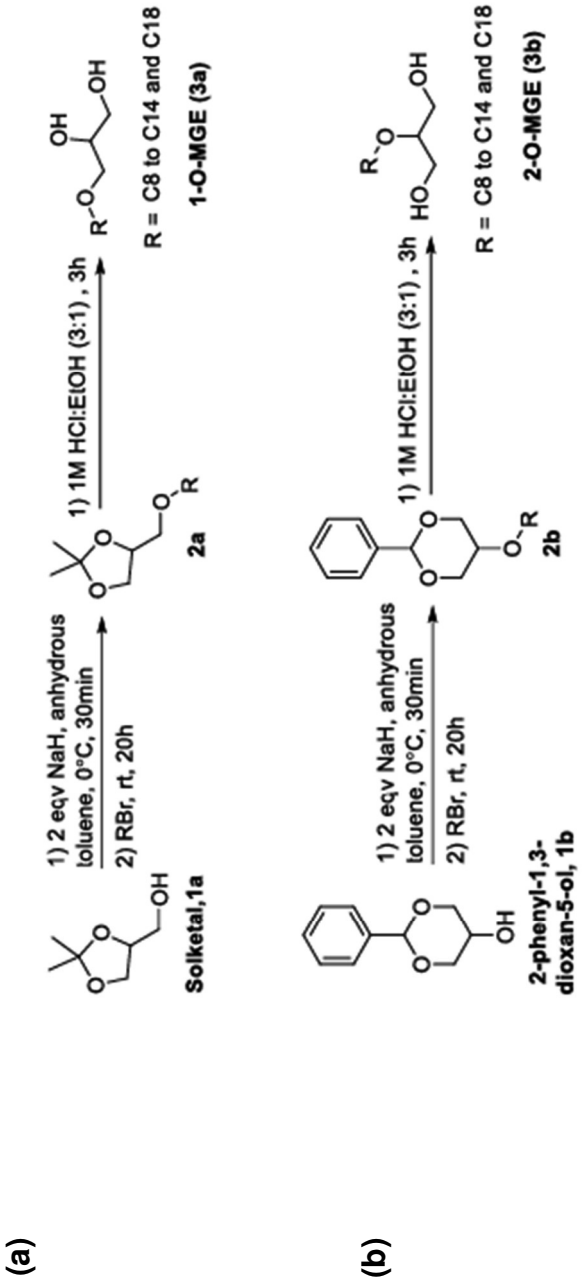
[Fig. 1]



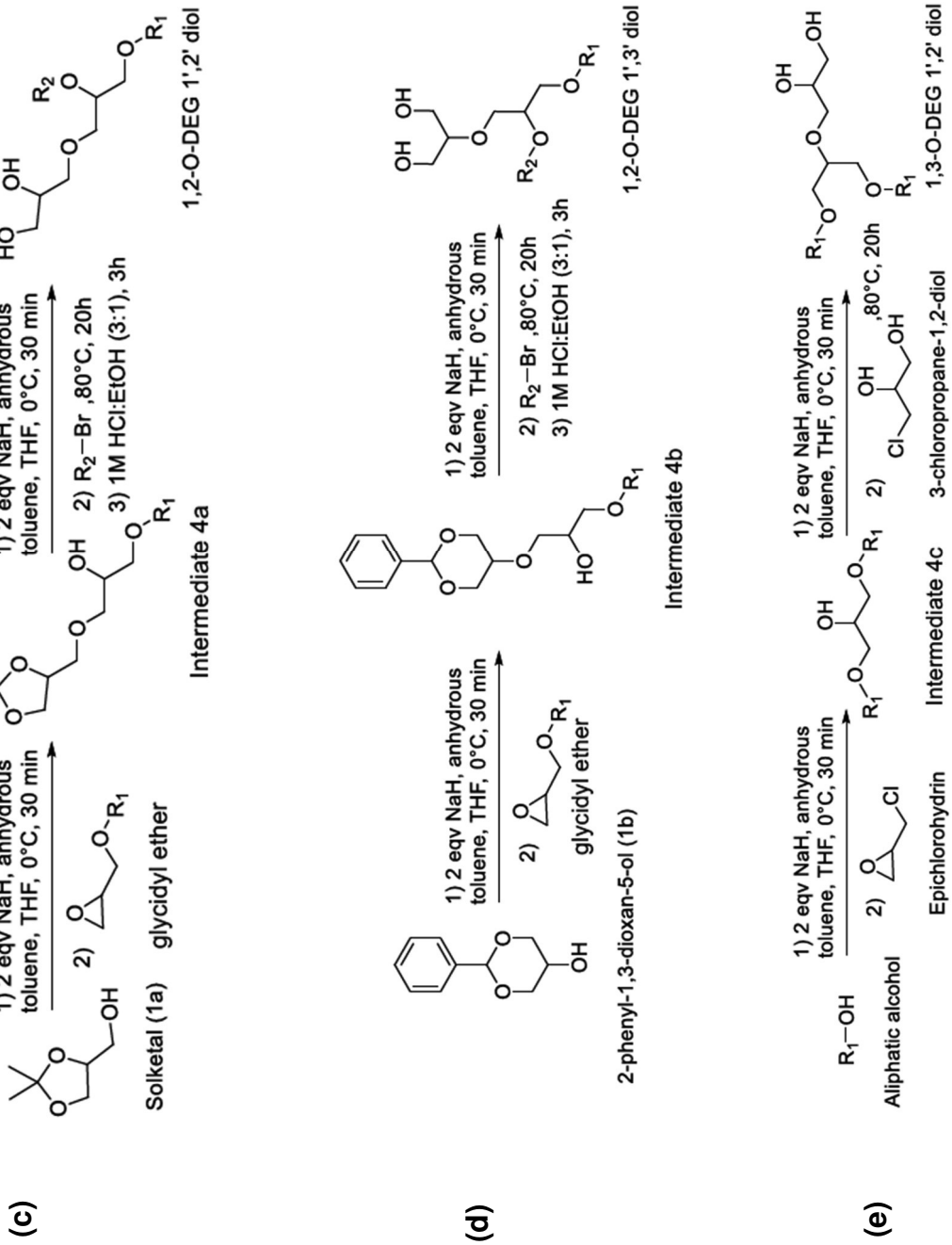
[Fig. 1] cont.


(b)
or
1) Williamson ether synthesis with RBr
2) Acidification using HCl
or
Solketal
2-phenyl-1,3-dioxan-5-ol
1-O-MGE
2-O-MGE
(c)
polymerization
1-O-MGE
1-O-MGE BBP
(d)
polymerization
2-O-MGE
2-O-MGE BBP
(e)
backbone chain length in diacid= n
branch chain length = m

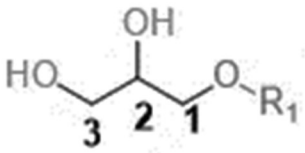
[Fig. 2]


(a)
1) 2 eqv NaH, anhydrous toluene, 0°C, 30min
2) RBr, rt, 20h
Solketal,1a
2a
1) 1M HCl:EtOH (3:1) , 3h
R = C8 to C14 and C18
1-O-MGE (3a)
(b)
1) 2 eqv NaH, anhydrous toluene, 0°C, 30min
2) RBr, rt, 20h
2-phenyl-1,3-dioxan-5-ol, 1b
2b
1) 1M HCl:EtOH (3:1) , 3h
R = C8 to C14 and C18
2-O-MGE (3b)

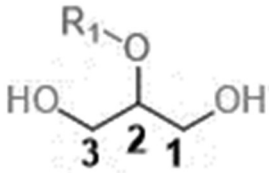
[Fig. 2] cont.


(c)
1) 2 eqv NaH, anhydrous toluene, THF, 0°C, 30 min
2)
Solketal (1a)
glycidyl ether
Intermediate 4a
2) R2−Br ,80°C, 20h
3) 1M HCl:EtOH (3:1), 3h
1,2-O-DEG 1',2' diol
(d)
2-phenyl-1,3-dioxan-5-ol (1b)
Intermediate 4b
1,2-O-DEG 1',3' diol
(e)
R1−OH
Aliphatic alcohol
Epichlorohydrin
Intermediate 4c
3-chloropropane-1,2-diol
1,3-O-DEG 1',2' diol

[Fig. 3]

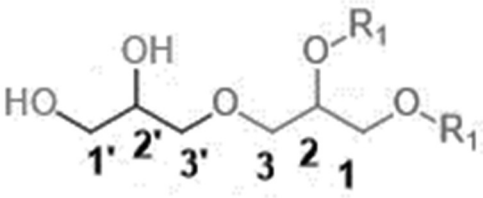


1-O-MGE

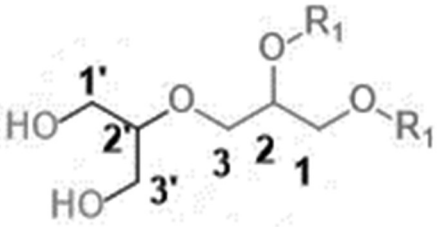


2-O-MGE

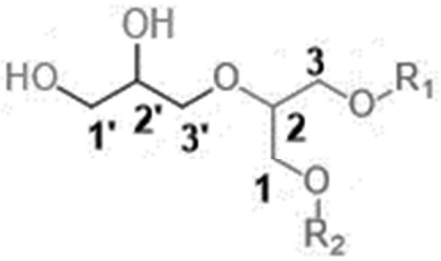
(3002)



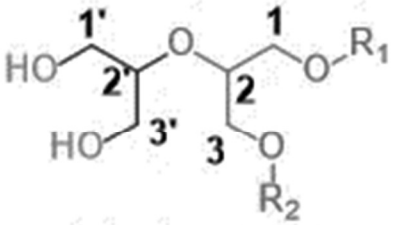
1,2-O-DGE 1',2' diol



1,2-O-DGE 1',3' diol



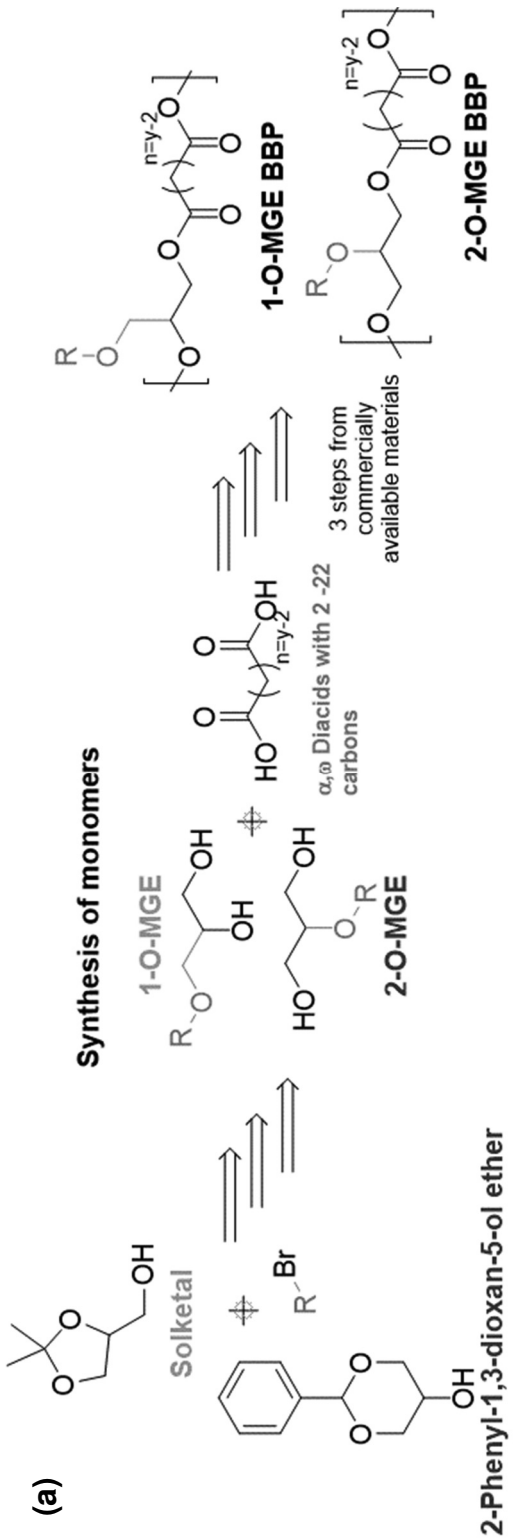
1,3-O-DGE 1',2' diol



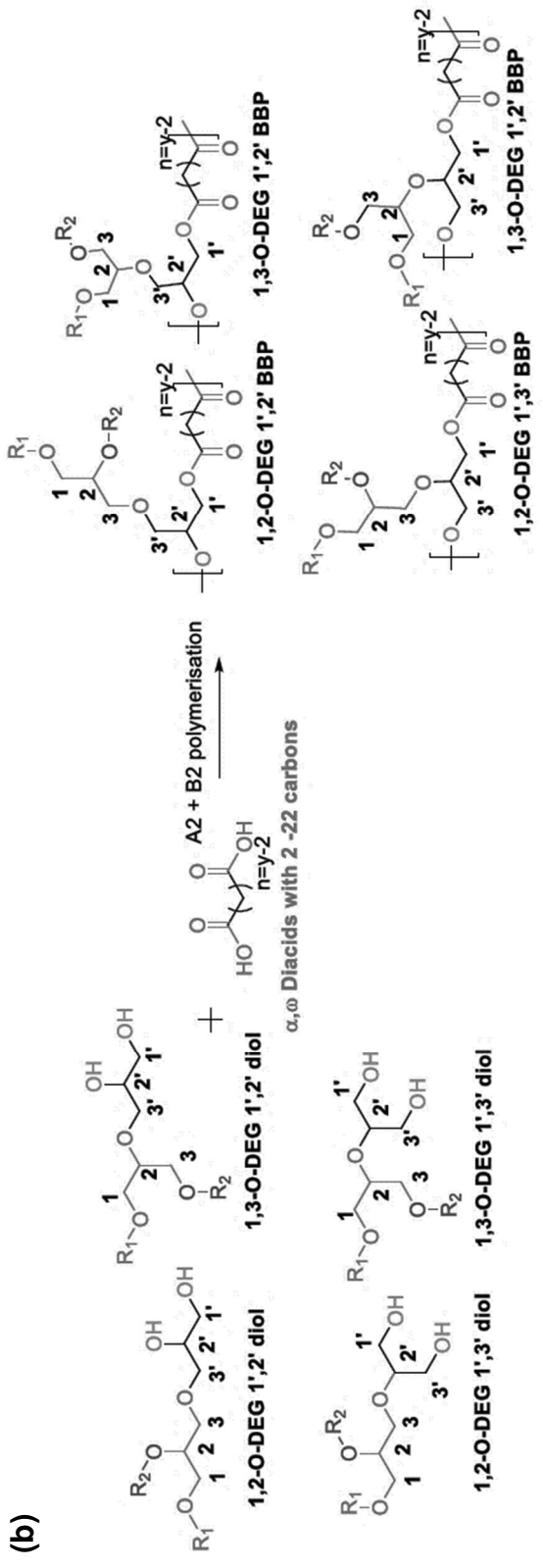
1,3-O-DGE 1',3' diol

(3004)

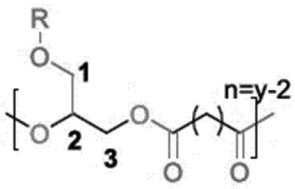
[Fig. 4]


(a)
Solketal
2-Phenyl-1,3-dioxan-5-ol ether
Synthesis of monomers
1-O-MGE
2-O-MGE
α,ω Diacids with 2 -22 carbons
3 steps from commercially available materials
1-O-MGE BBP
2-O-MGE BBP

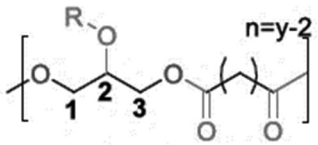
[Fig. 4] cont.


(b)
1,2-O-DEG 1',2' diol
1,3-O-DEG 1',2' diol
1,2-O-DEG 1',3' diol
1,3-O-DEG 1',3' diol
α,ω Diacids with 2 -22 carbons
A2 + B2 polymerisation
1,2-O-DEG 1',2' BBP
1,3-O-DEG 1',2' BBP
1,2-O-DEG 1',3' BBP
1,3-O-DEG 1',3' BBP

[Fig. 5]

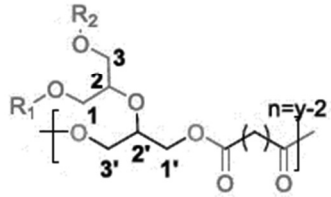


1-O-MGE BBP

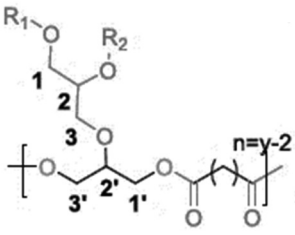


2-O-MGE BBP

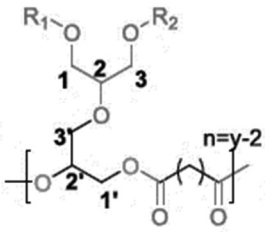
(6002)



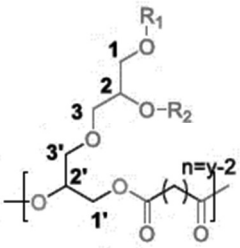
1,3-O-DEG 1',3' BBP



1,2-O-DEG 1',3' BBP



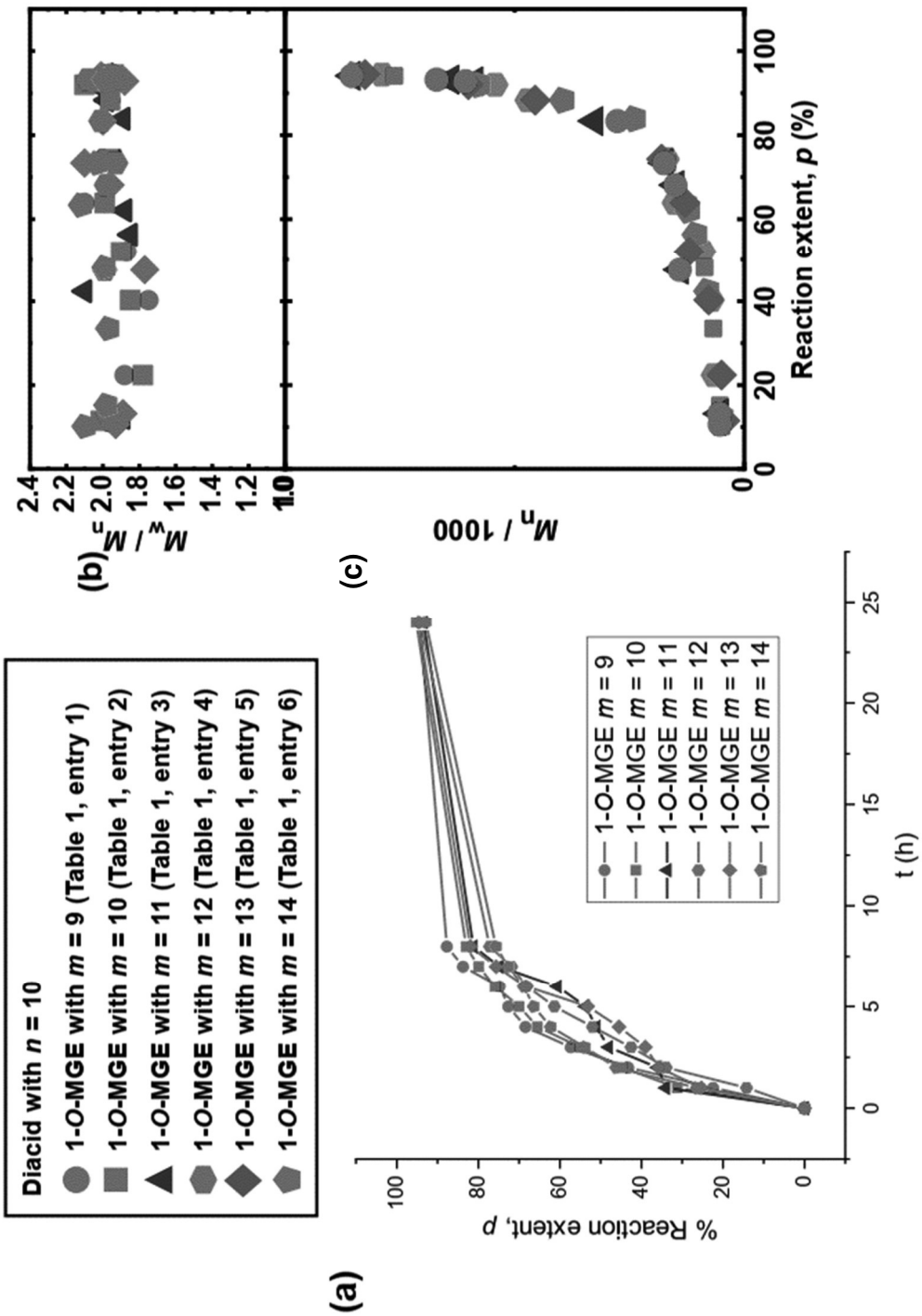
1,3-O-DEG 1',2' BBP



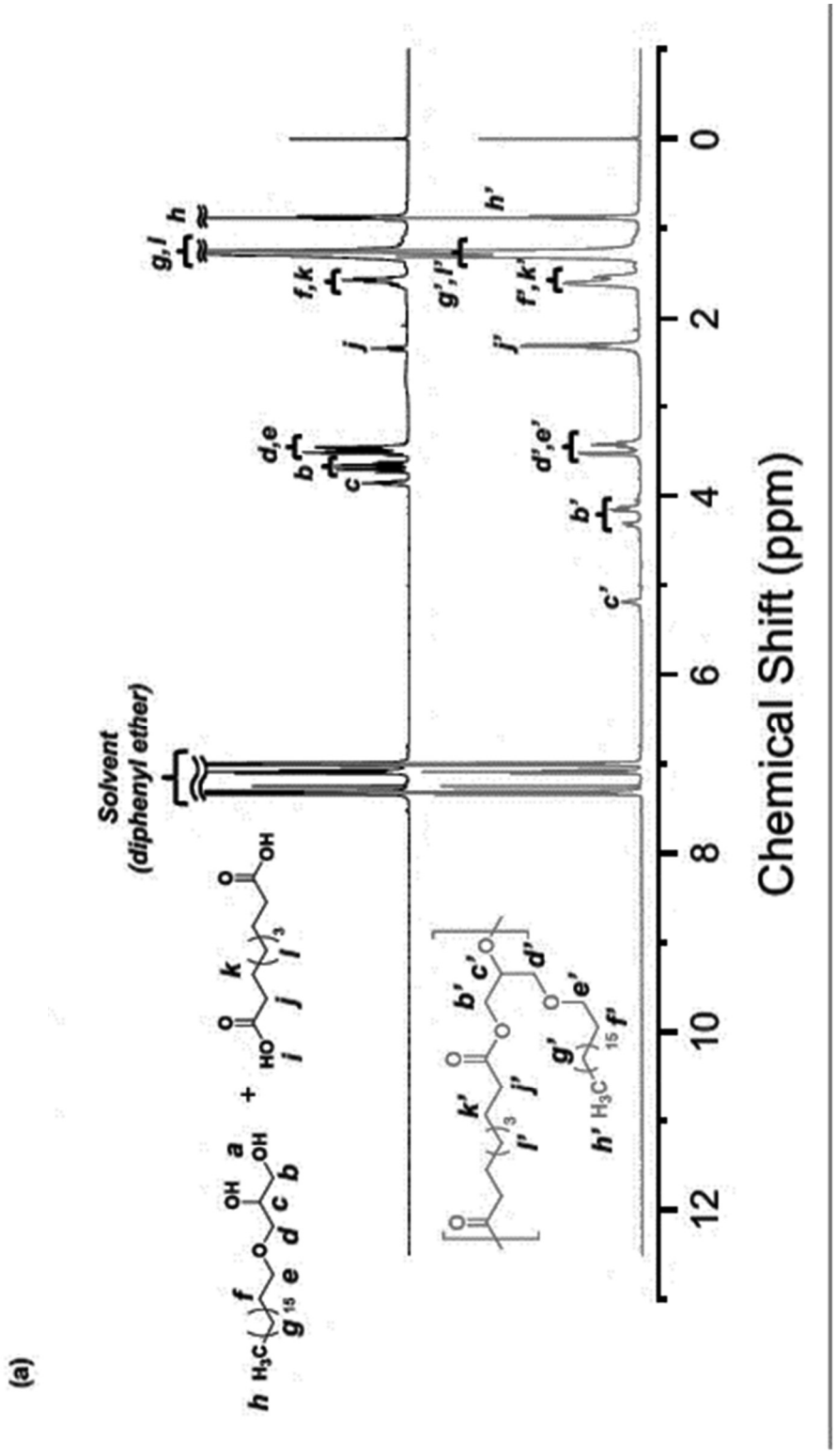
1,2-O-DEG 1',2' BBP

(6004)

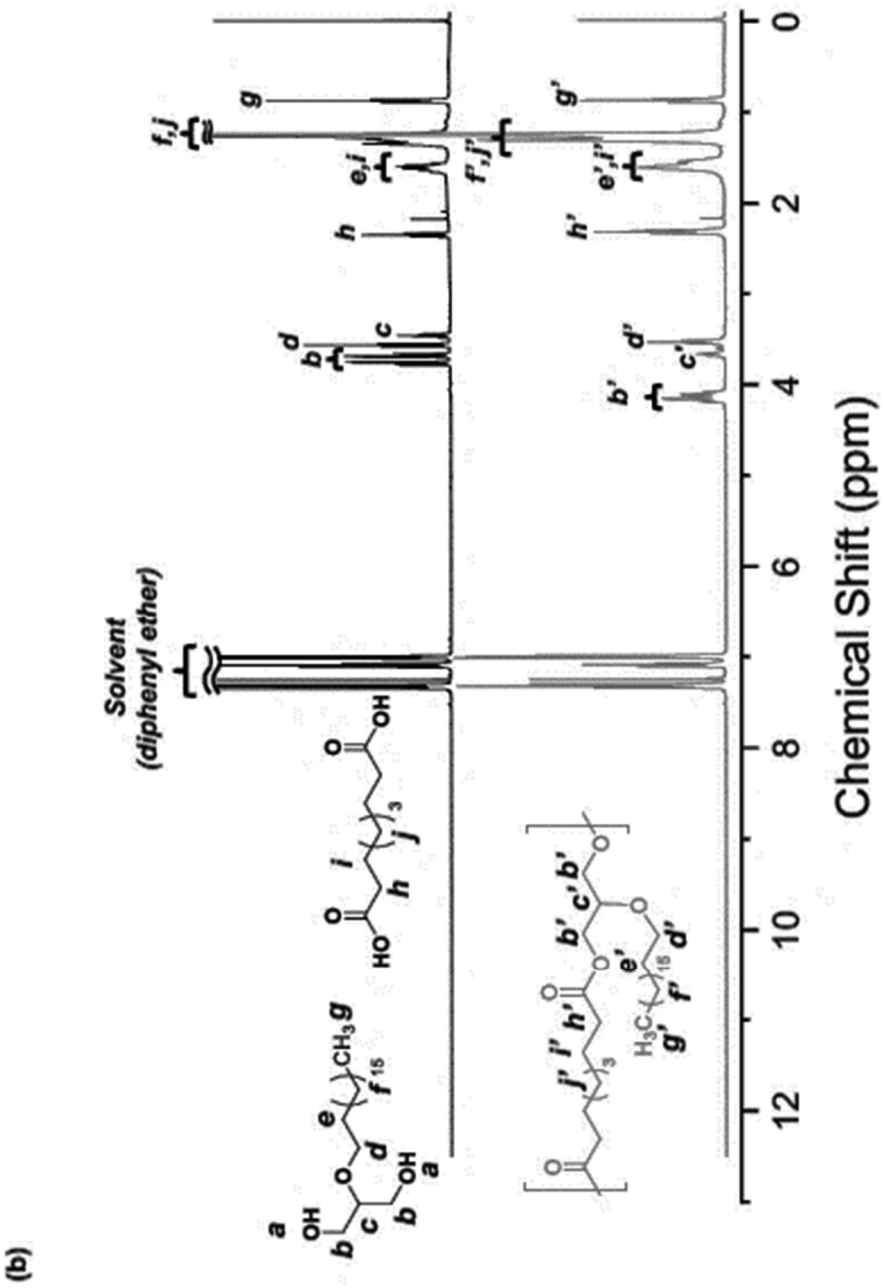
[Fig. 6]


Diacid with n = 10
1-O-MGE with m = 9 (Table 1, entry 1)
1-O-MGE with m = 10 (Table 1, entry 2)
1-O-MGE with m = 11 (Table 1, entry 3)
1-O-MGE with m = 12 (Table 1, entry 4)
1-O-MGE with m = 13 (Table 1, entry 5)
1-O-MGE with m = 14 (Table 1, entry 6)
(a)
% Reaction extent, p
t (h)
1-O-MGE m = 9
1-O-MGE m = 10
1-O-MGE m = 11
1-O-MGE m = 12
1-O-MGE m = 13
1-O-MGE m = 14
(b)
Mw / Mn
(c)
Mn / 1000
Reaction extent, p (%)

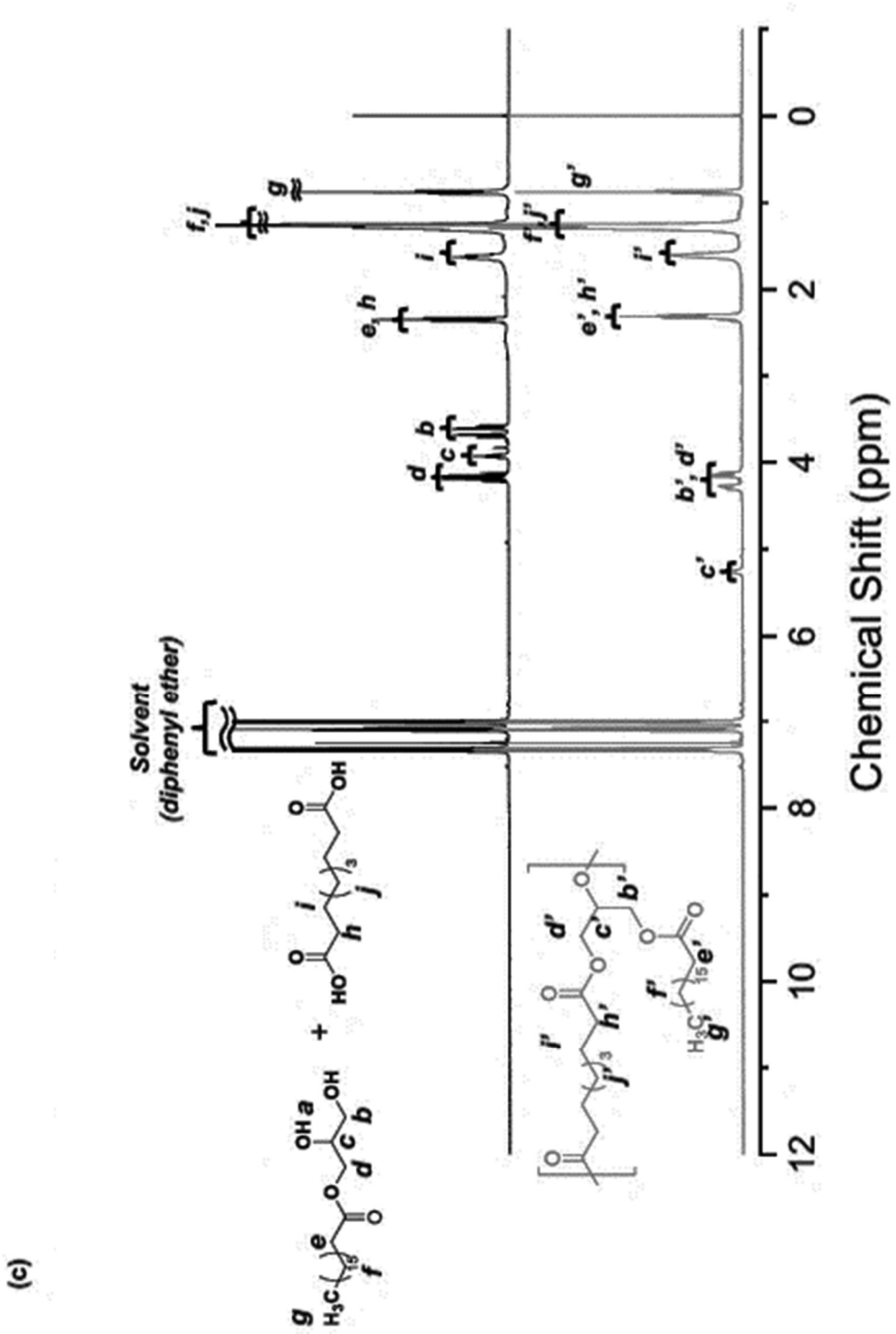
[Fig. 7]



[Fig. 7] cont.

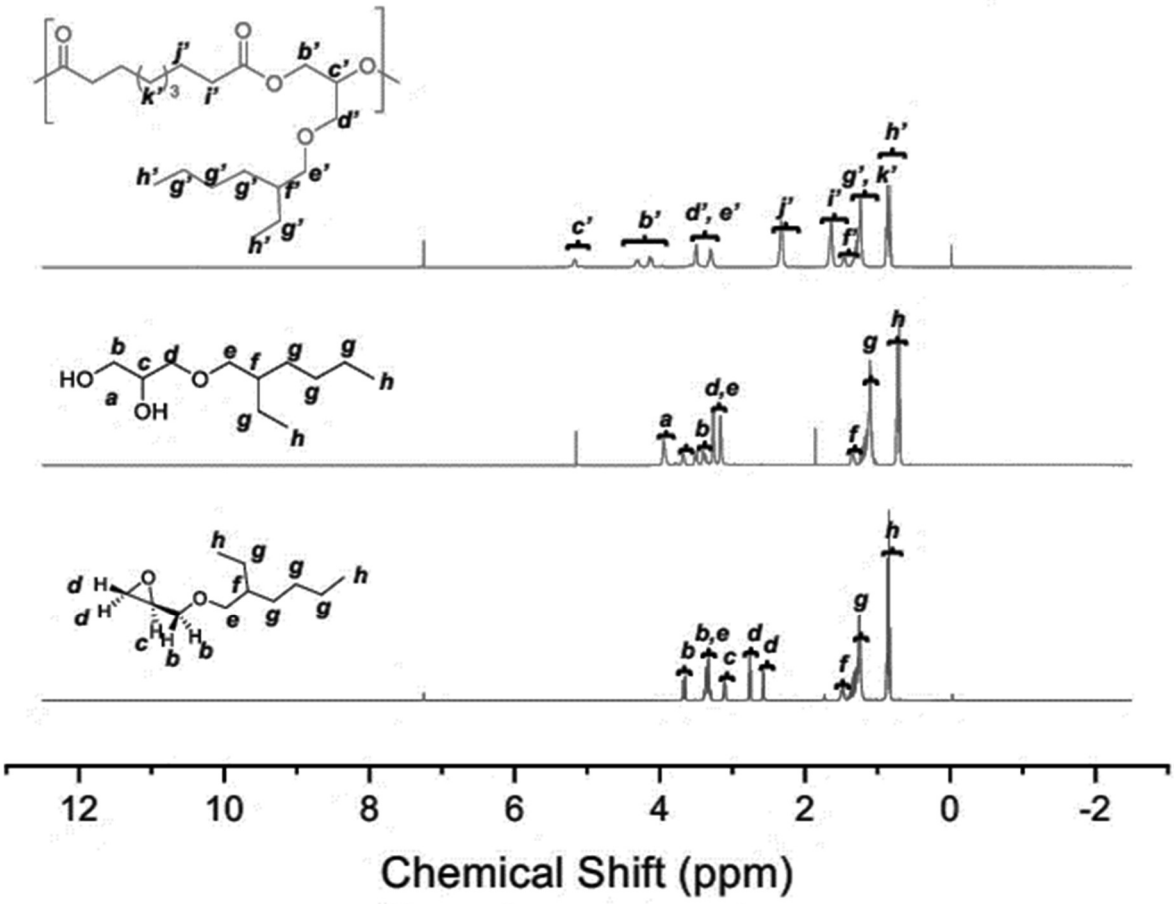


[Fig. 7] cont.



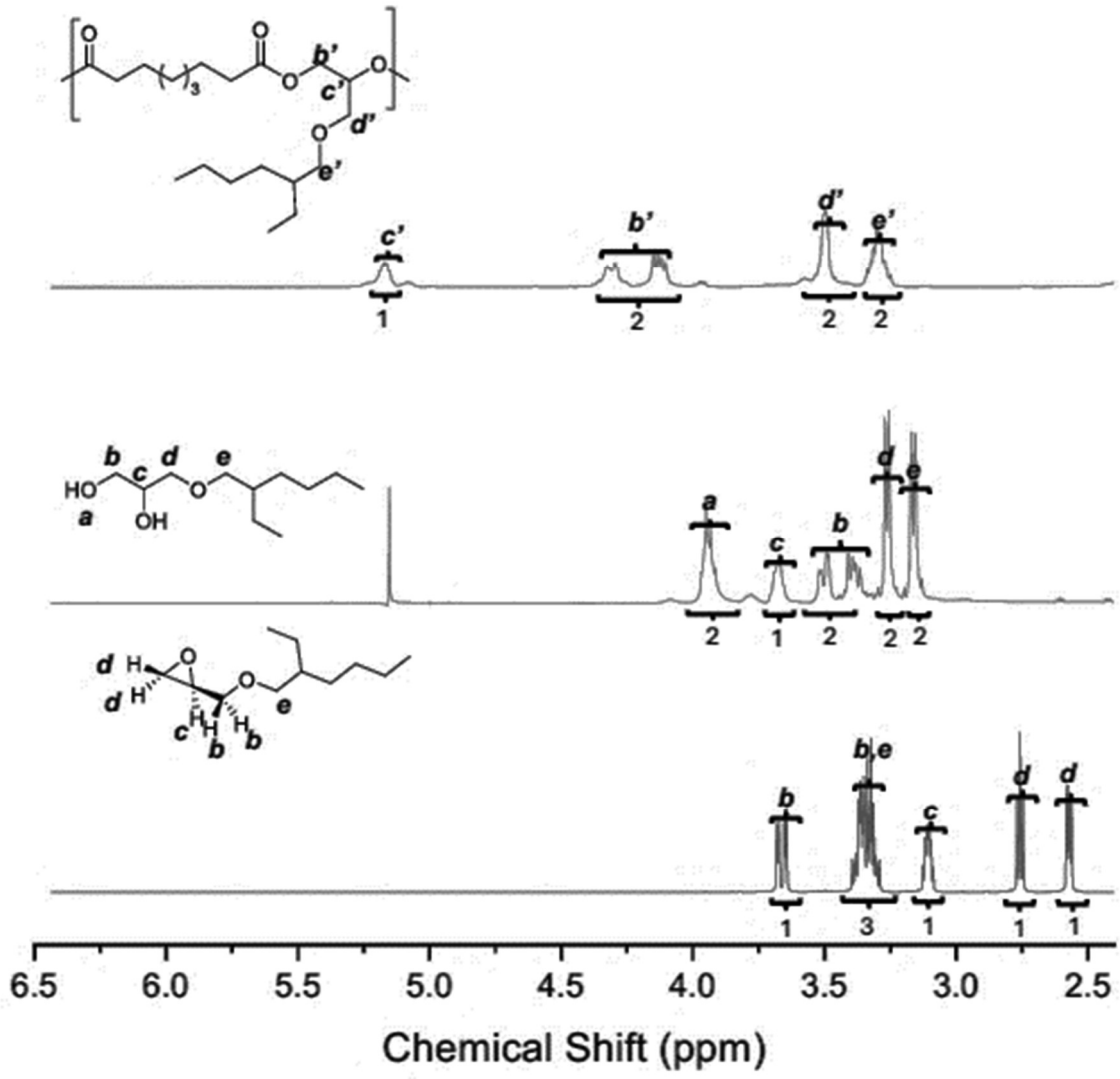
[Fig. 7] cont.

(d)

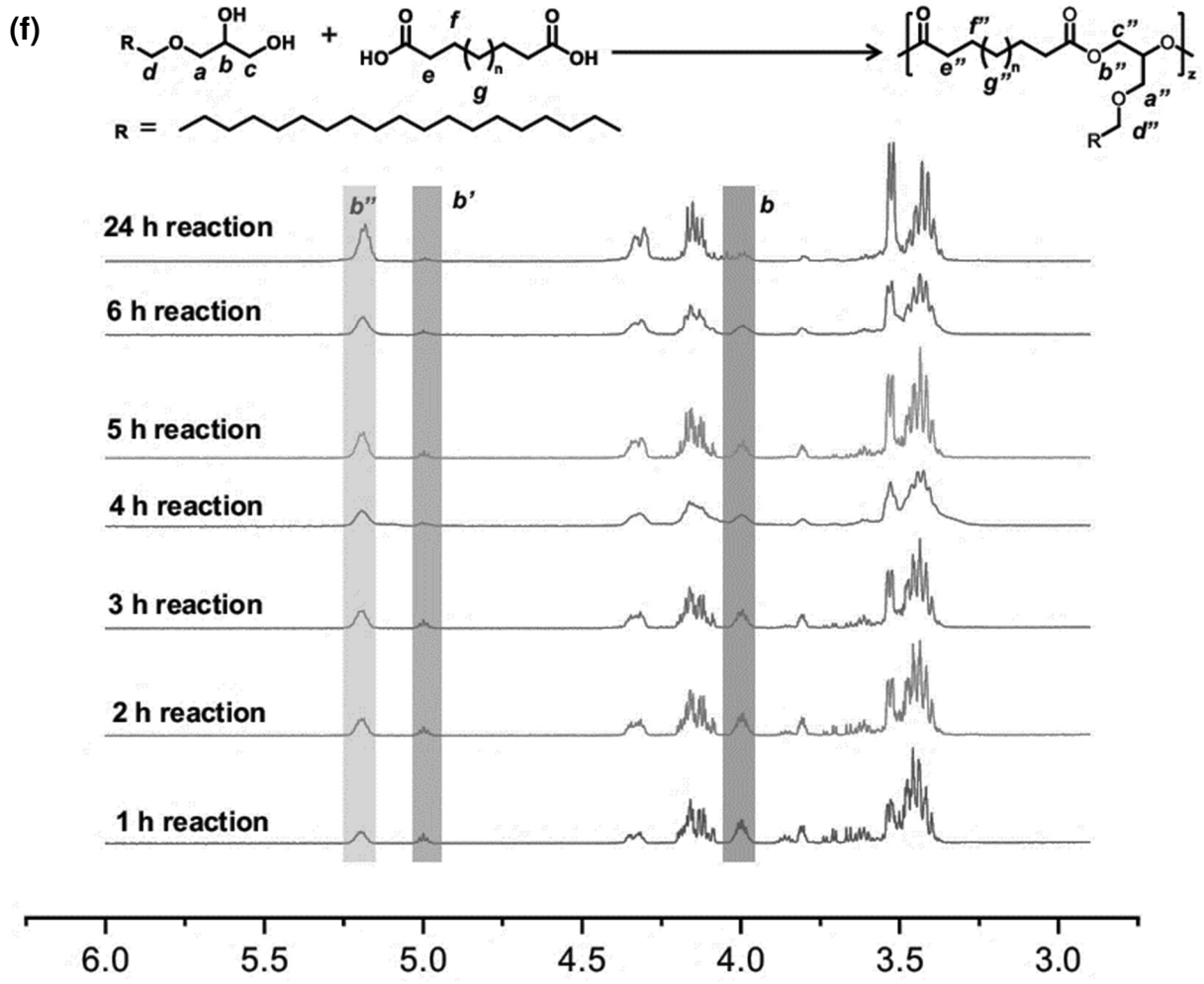


[Fig. 7] cont.

(e)

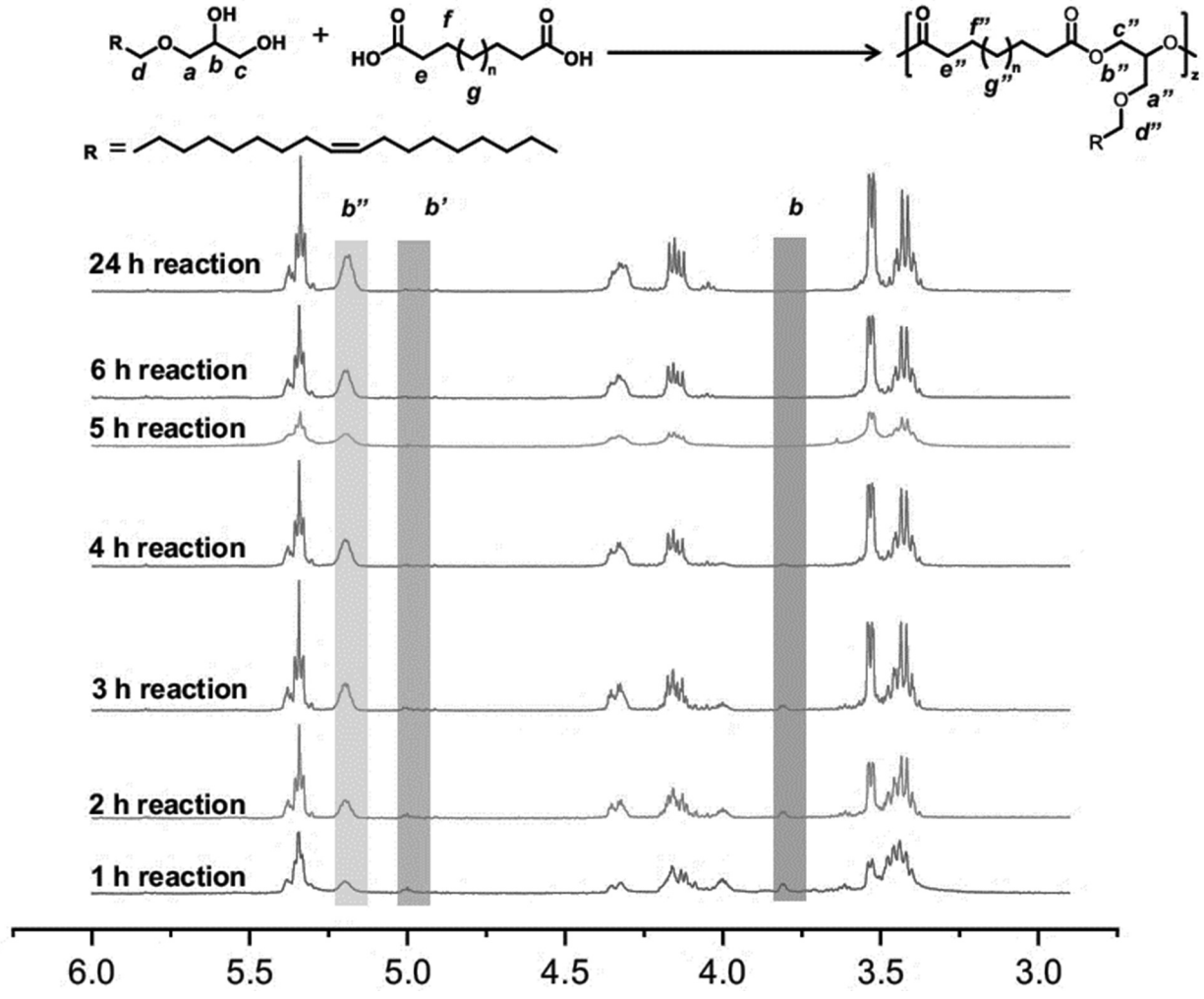

c'
b'
d'
e'
1
2
2
2
a
b
c
d
e
2
1
2
2
2
b
e
d
1
3
1
1
1
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
Chemical Shift (ppm)

[Fig. 7] cont.

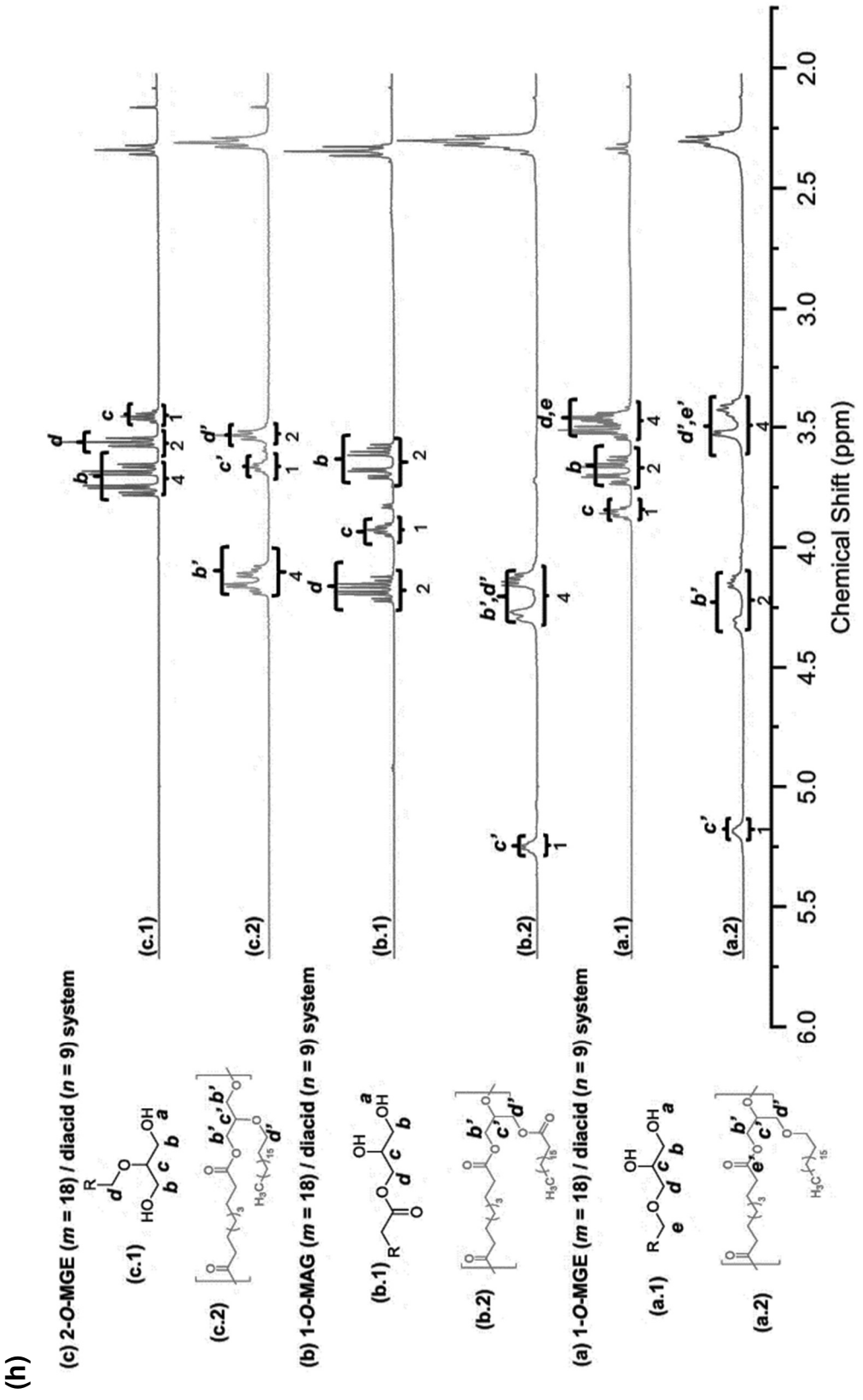

(f)
R =
24 h reaction
6 h reaction
5 h reaction
4 h reaction
3 h reaction
2 h reaction
1 h reaction
b''
b'
b
6.0
5.5
5.0
4.5
4.0
3.5
3.0

[Fig. 7] cont.

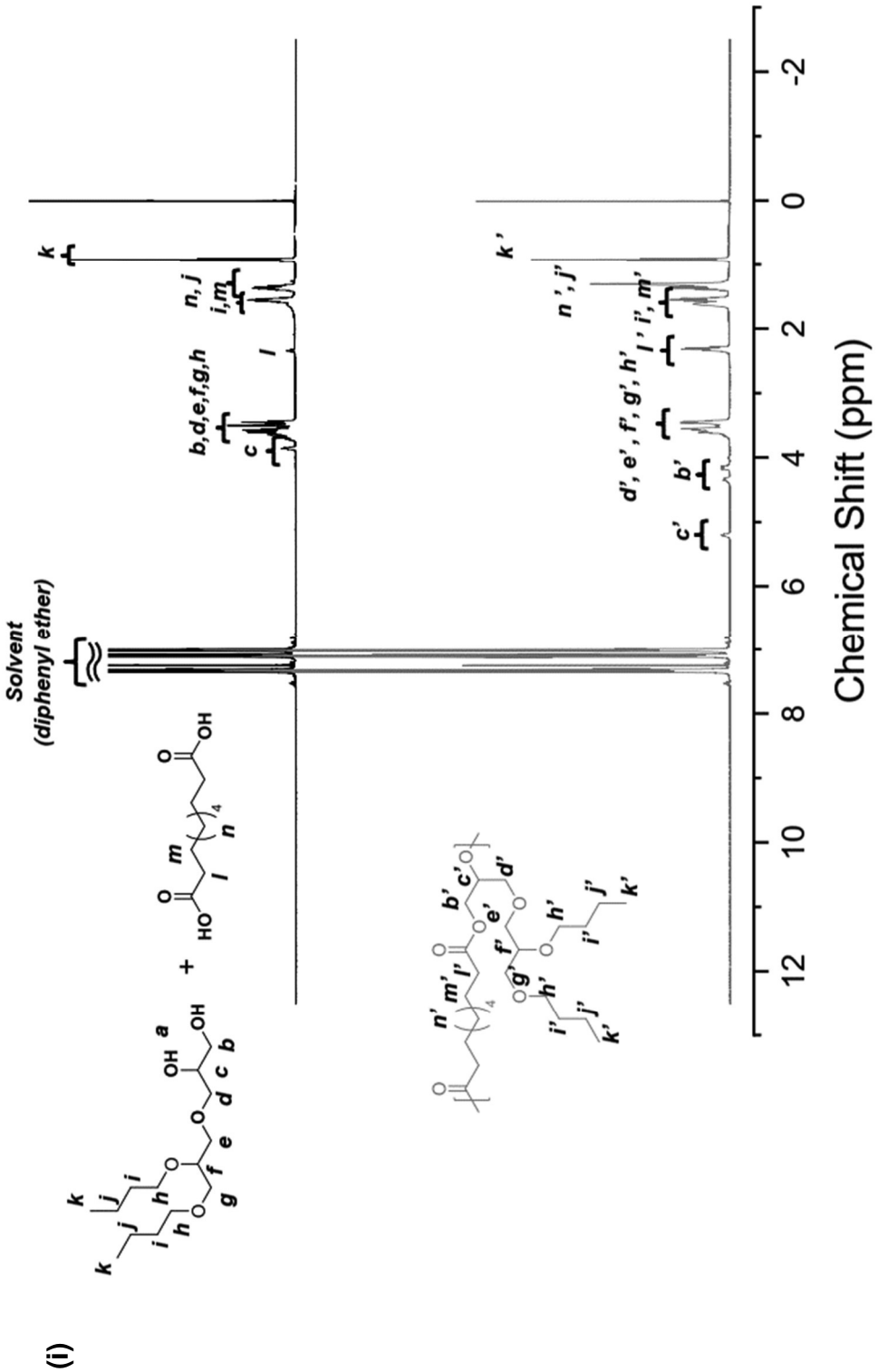
(g)


R =
b''
b'
b
24 h reaction
6 h reaction
5 h reaction
4 h reaction
3 h reaction
2 h reaction
1 h reaction
6.0
5.5
5.0
4.5
4.0
3.5
3.0

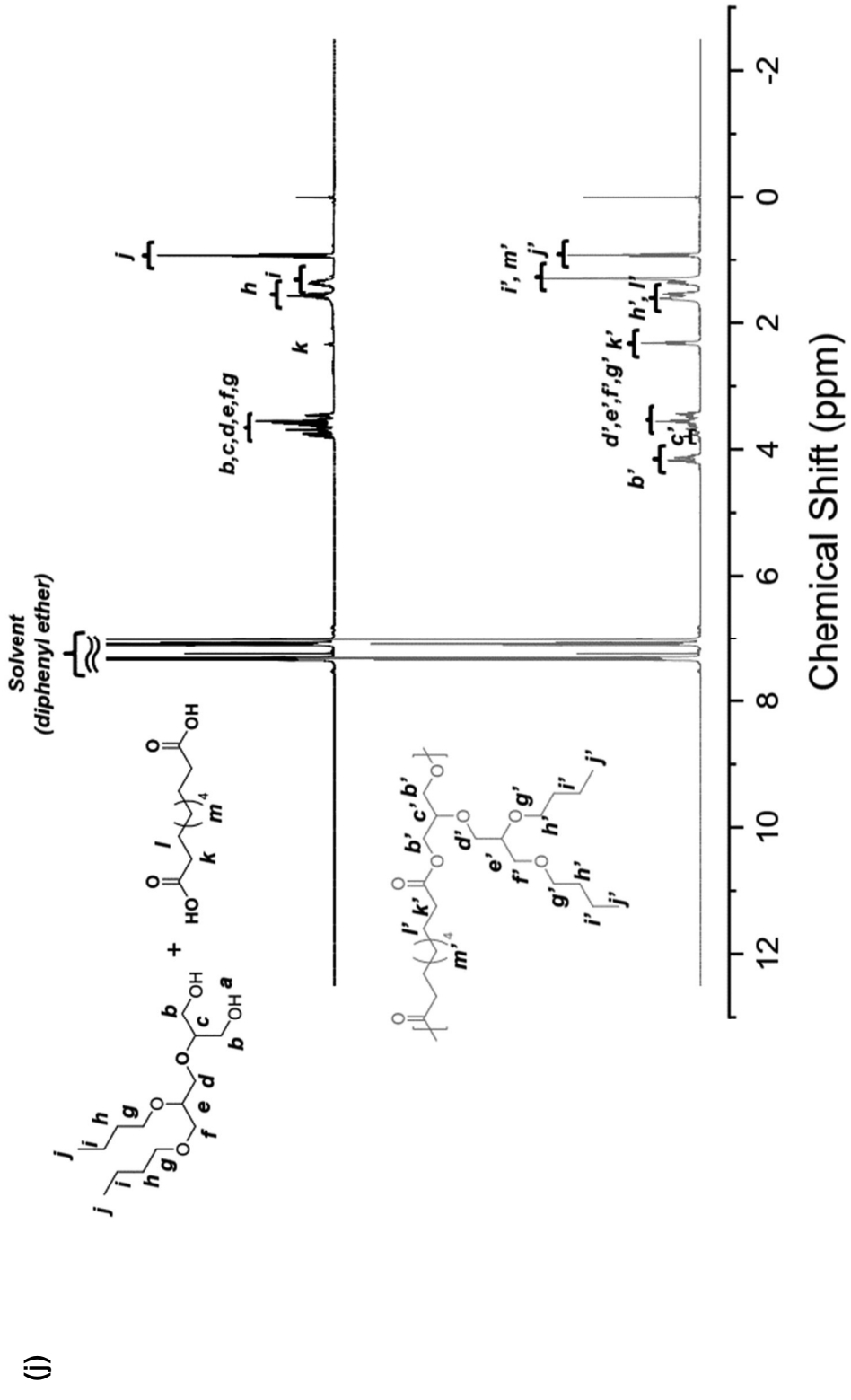
[Fig. 7] cont.


(h)
(c) 2-O-MGE (m = 18) / diacid (n = 9) system
(c.1)
(c.2)
(b) 1-O-MAG (m = 18) / diacid (n = 9) system
(b.1)
(b.2)
(a) 1-O-MGE (m = 18) / diacid (n = 9) system
(a.1)
(a.2)
Chemical Shift (ppm)
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0

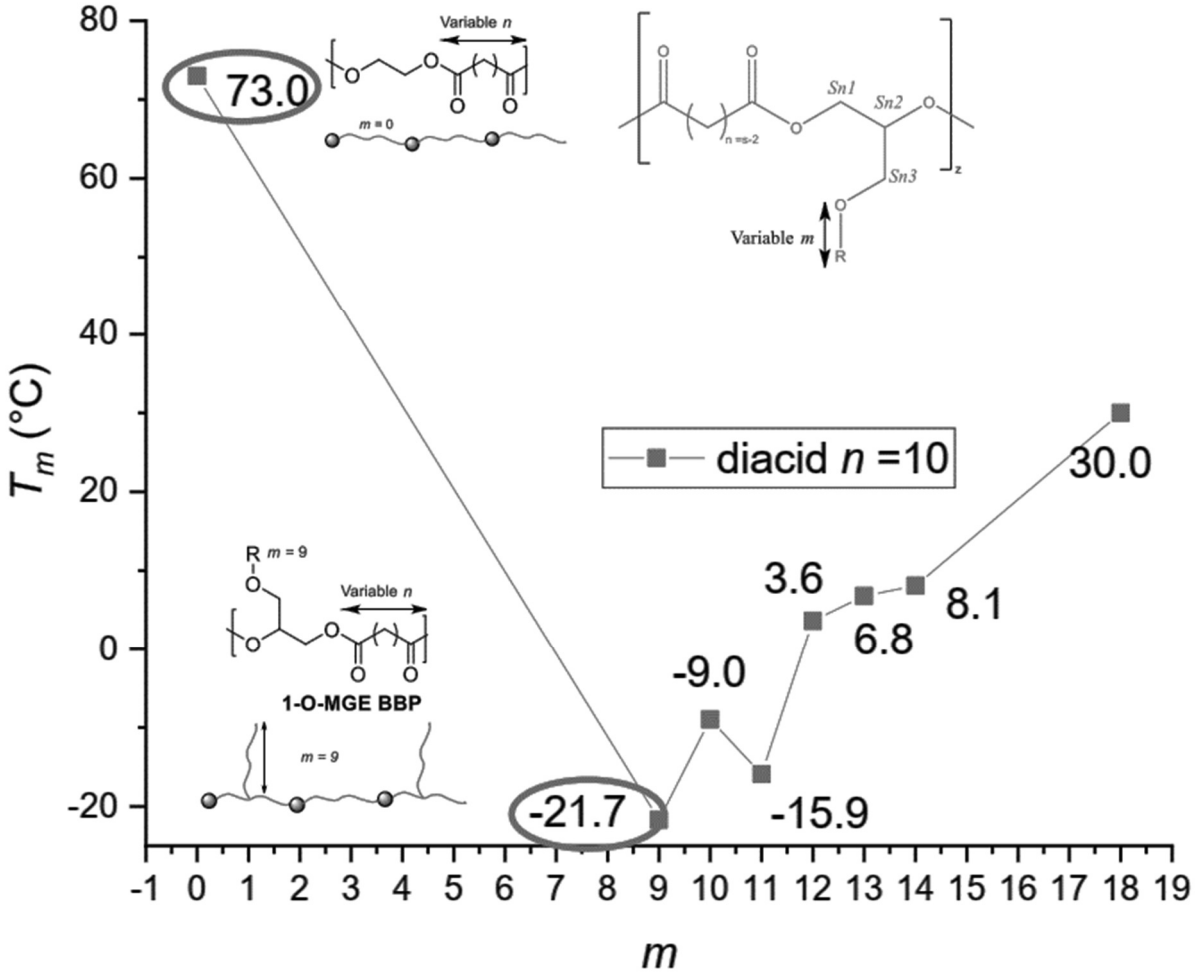
[Fig. 7] cont.



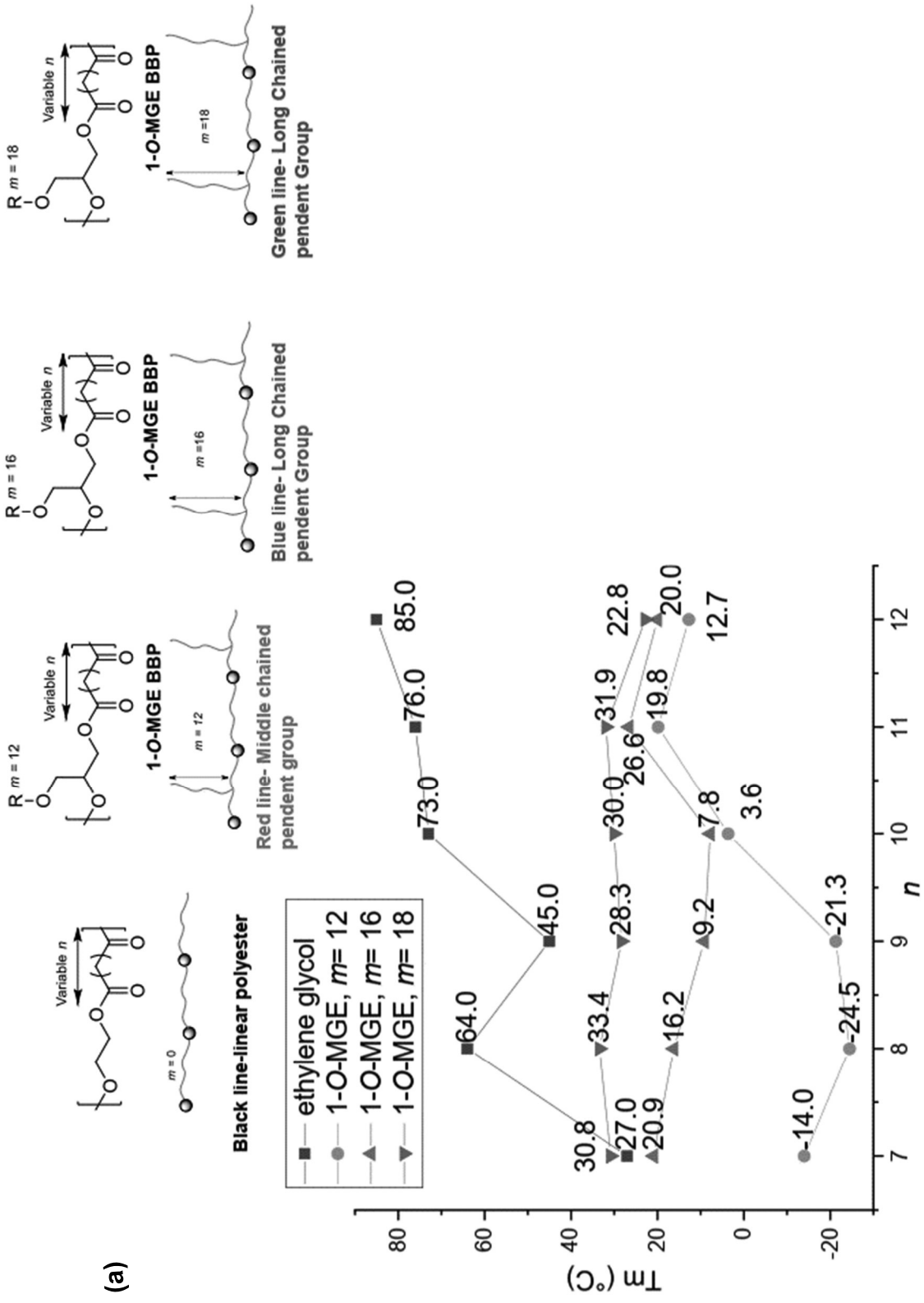
[Fig. 7] cont.


(i)
Solvent
(diphenyl ether)
b,c,d,e,f,g
h
i
j
k
b'
d',e',f',g' k'
h', l'
i', m'
j'
Chemical Shift (ppm)
12
10
8
6
4
2
0
-2

[Fig. 8]

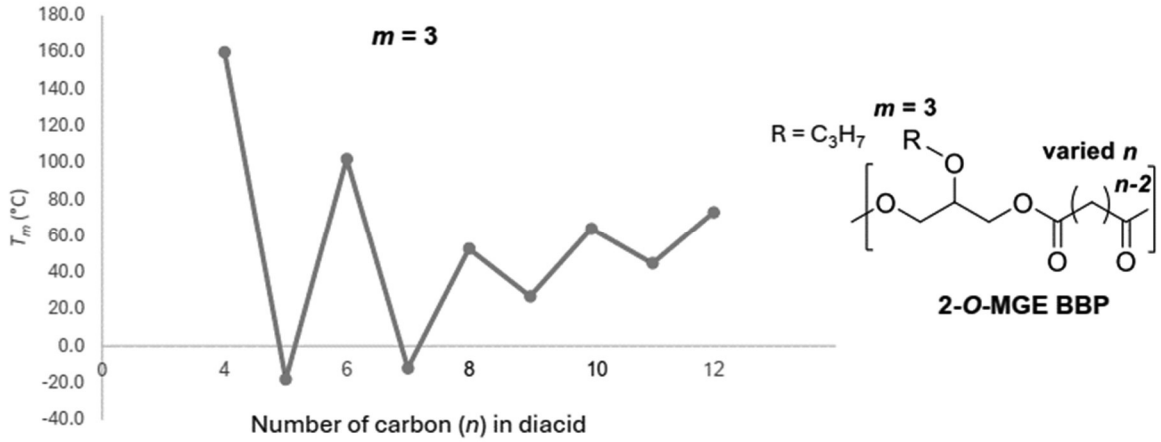

80
60
40
20
0
-20
T_m (°C)
-1 0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19
m
73.0
-21.7
-9.0
-15.9
3.6
6.8
8.1
30.0
diacid n =10
Variable n
m = 0
Sn1
Sn2
Sn3
Variable m
R
n =s-2
z
R m = 9
Variable n
1-O-MGE BBP
m = 9

[Fig. 9]

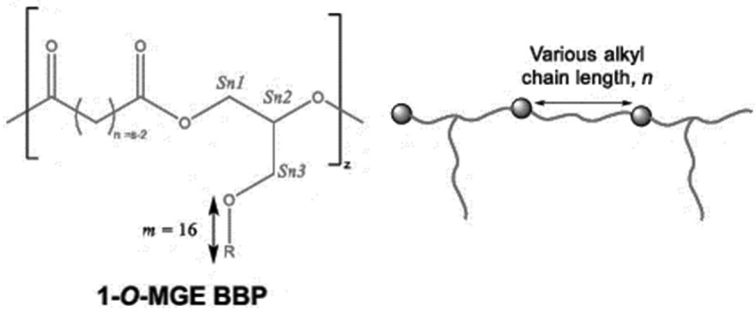

(a)
Variable n
m = 0
Black line-linear polyester
R m = 12
Variable n
1-O-MGE BBP
m = 12
Red line- Middle chained pendent group
R m = 16
Variable n
1-O-MGE BBP
m =16
Blue line- Long Chained pendent Group
R m = 18
Variable n
1-O-MGE BBP
m =18
Green line- Long Chained pendent Group
ethylene glycol
1-O-MGE, m= 12
1-O-MGE, m= 16
1-O-MGE, m= 18
Tm (°C)
n
85.0
76.0
73.0
64.0
45.0
30.8
27.0
20.9
33.4
16.2
28.3
9.2
30.0
26.6
31.9
19.8
22.8
7.8
20.0
12.7
3.6
-14.0
-24.5
-21.3

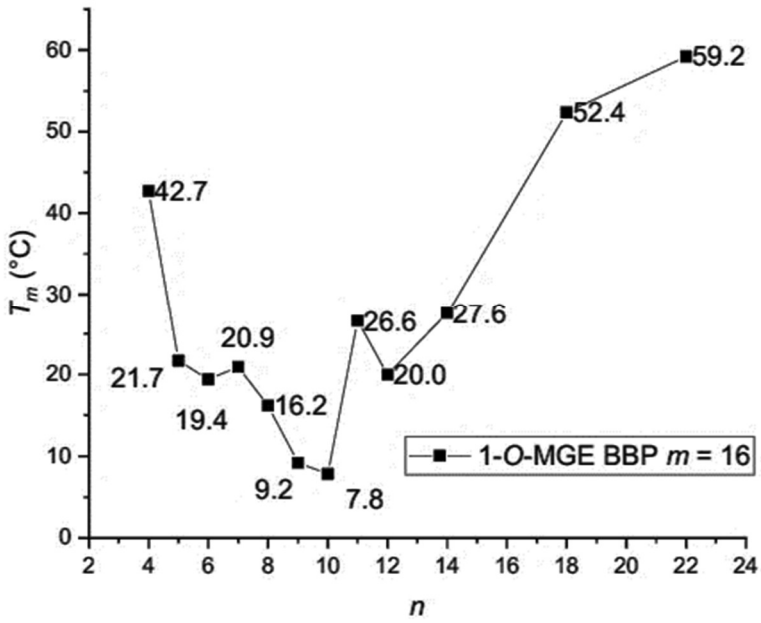
[Fig. 9] cont.

(b)

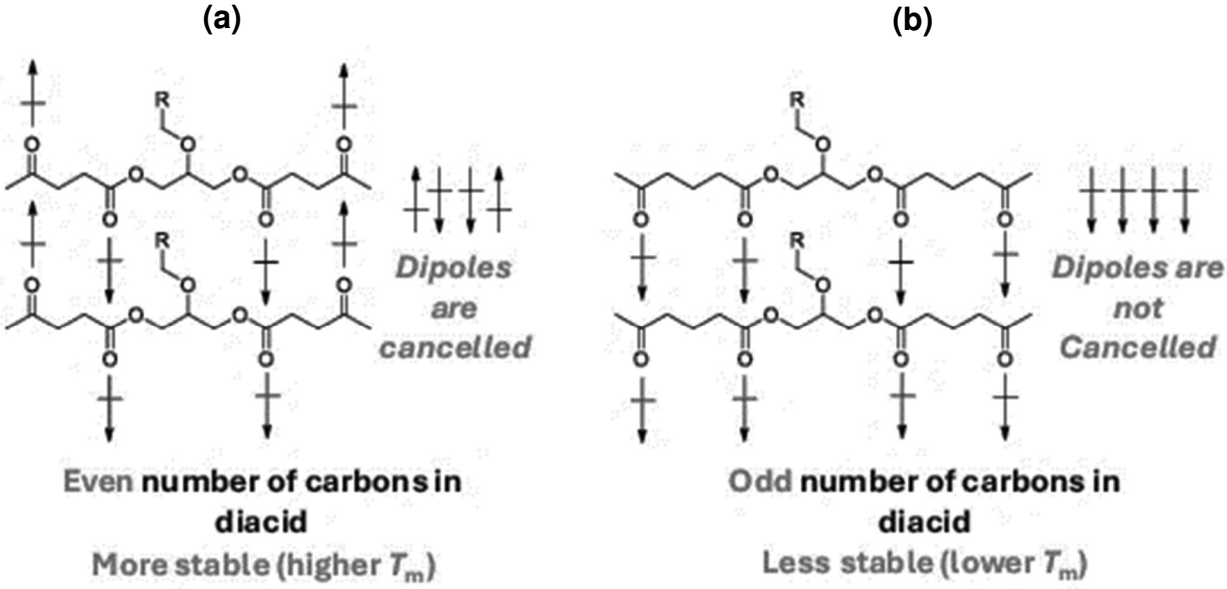

m = 3
T_m (°C)
Number of carbon (n) in diacid
m = 3
R = C_3H_7
varied n
n-2
2-O-MGE BBP

(c)


Sn1
Sn2
Sn3
m = 16
Various alkyl
chain length, n
1-O-MGE BBP

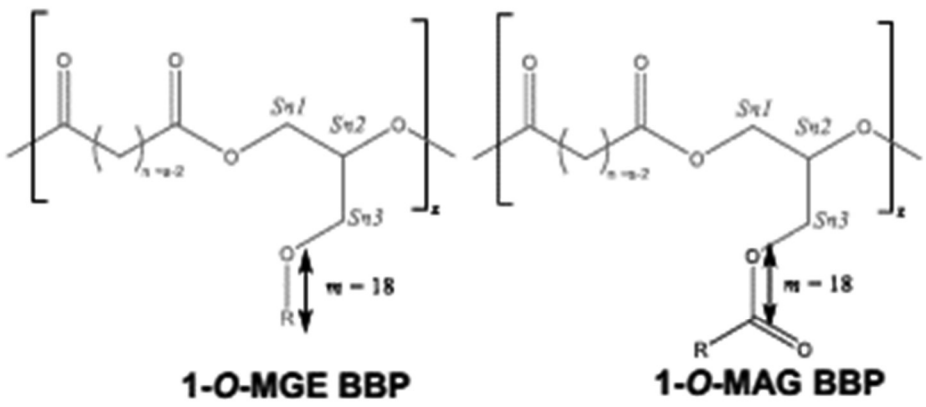

T_m (°C)
n
42.7
21.7
19.4
20.9
16.2
9.2
7.8
26.6
20.0
27.6
52.4
59.2
1-O-MGE BBP m = 16

[Fig. 10]

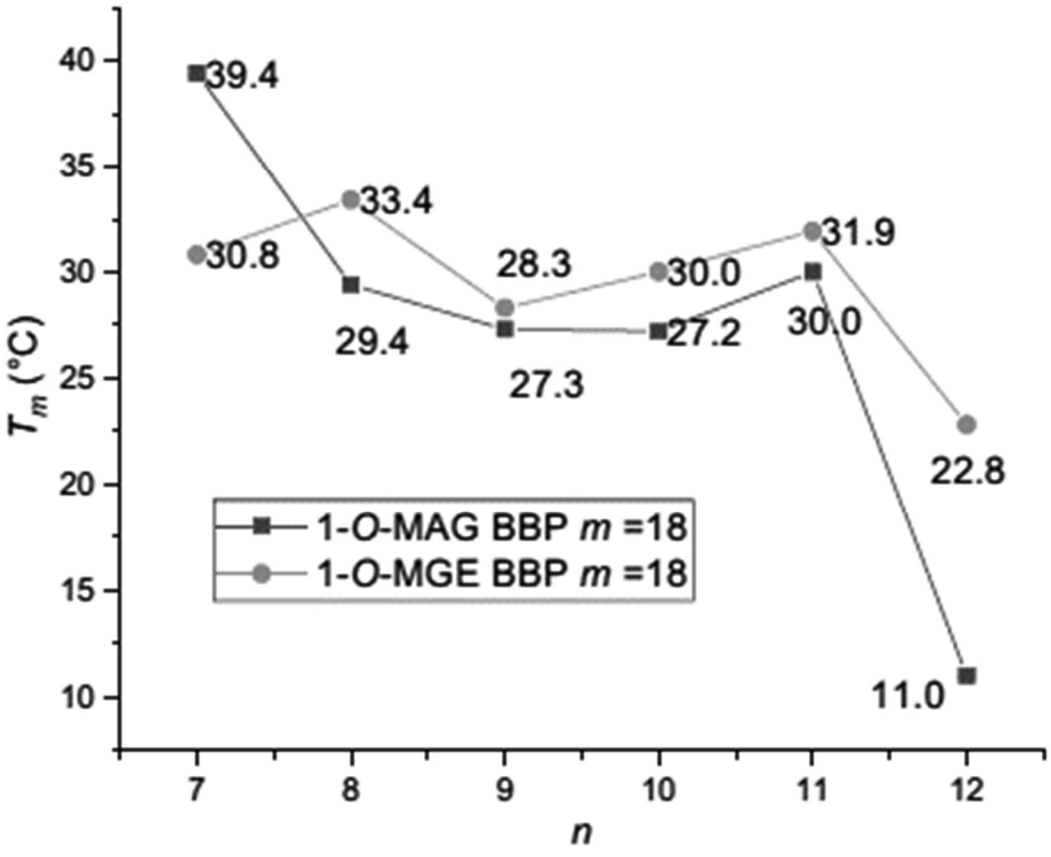

(a)
(b)
R
R
Dipoles are cancelled
R
R
Dipoles are not Cancelled
Even number of carbons in diacid
More stable (higher T_m)
Odd number of carbons in diacid
Less stable (lower T_m)

[Fig. 11]

(a)

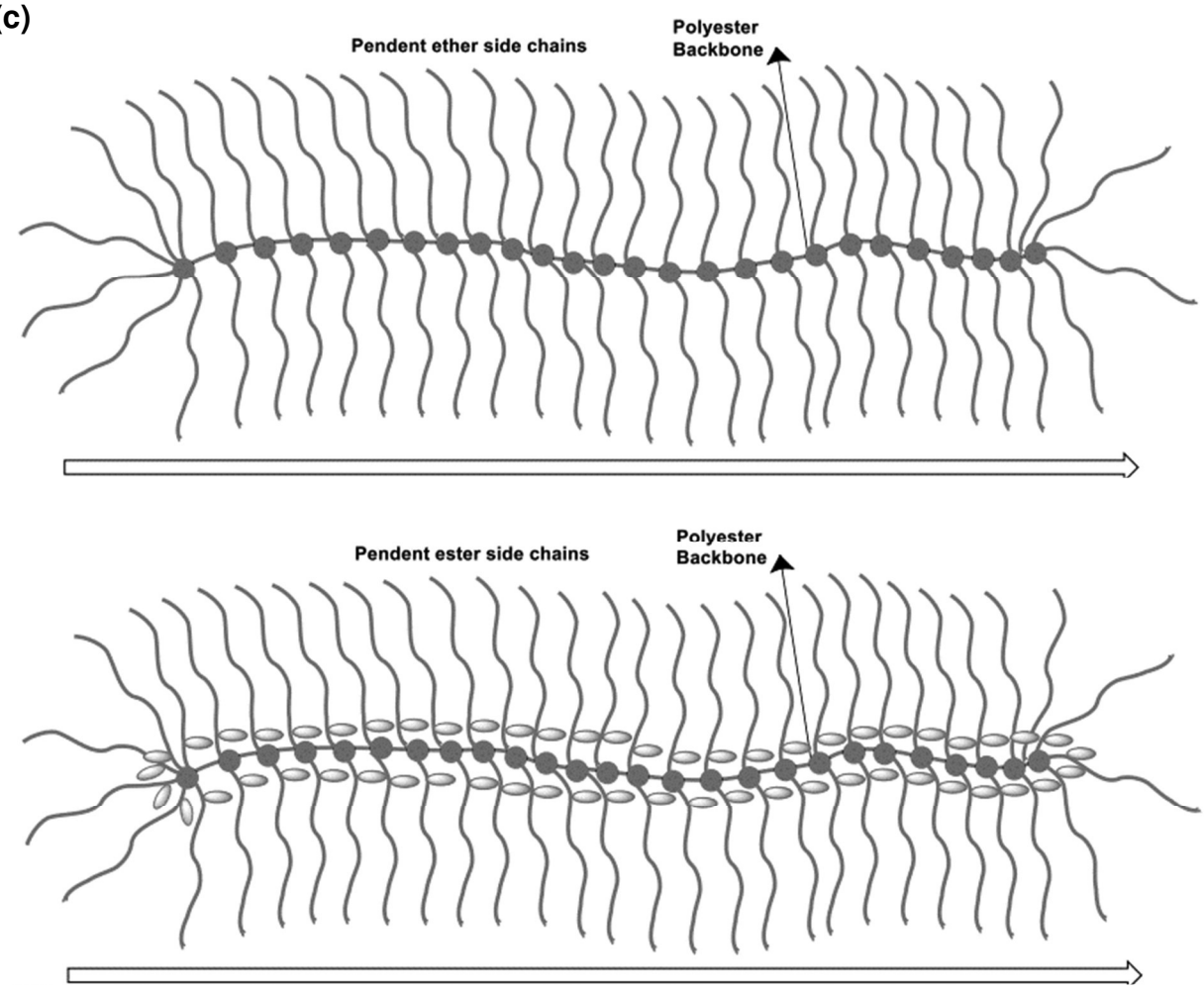

Sn1
Sn2
Sn3
m = 18
R
1-O-MGE BBP
1-O-MAG BBP

(b)

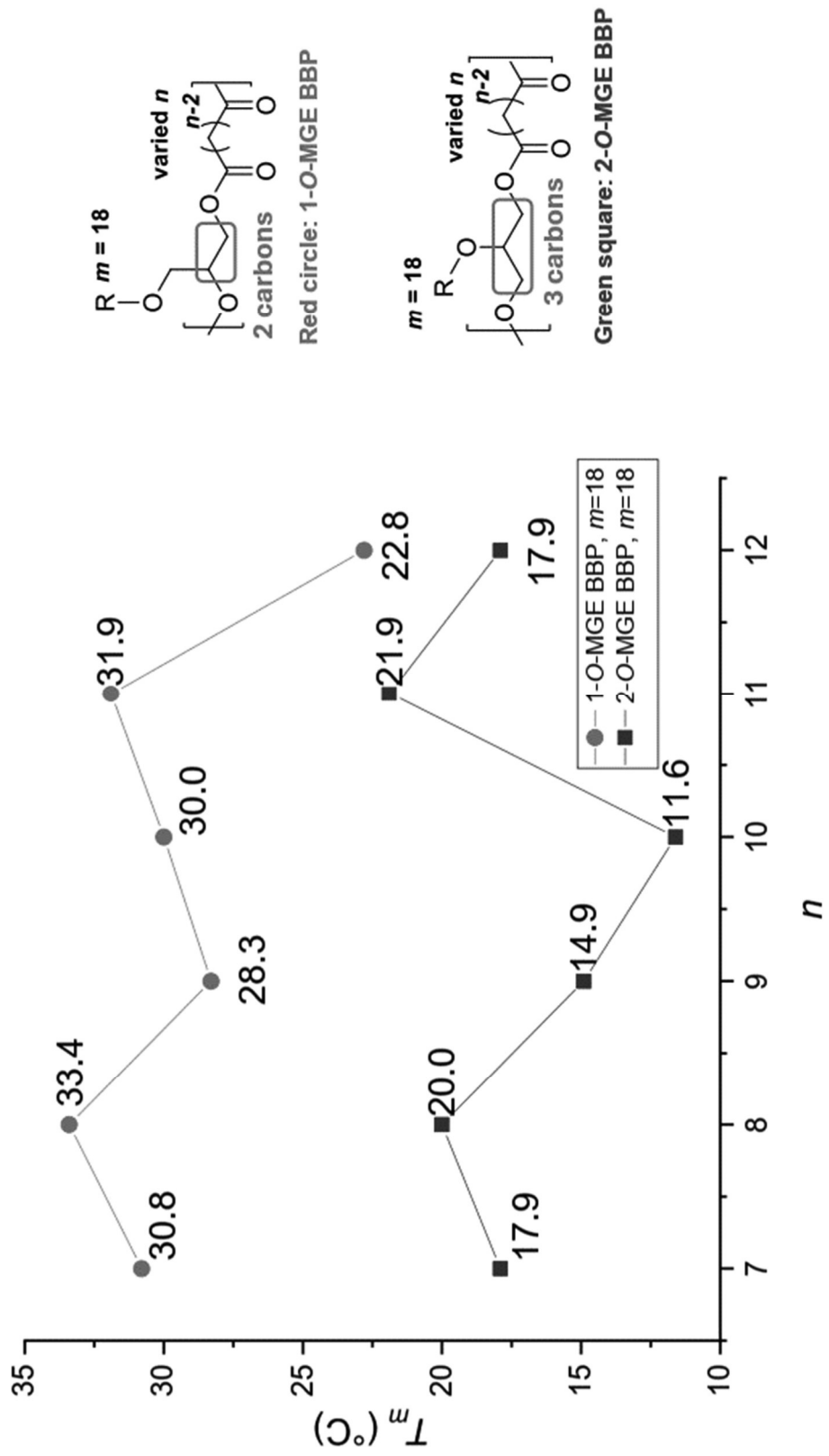

T_m (°C)
n
39.4
33.4
30.8
29.4
28.3
27.3
30.0
27.2
31.9
30.0
22.8
11.0
1-O-MAG BBP m =18
1-O-MGE BBP m =18

[Fig. 11] cont.

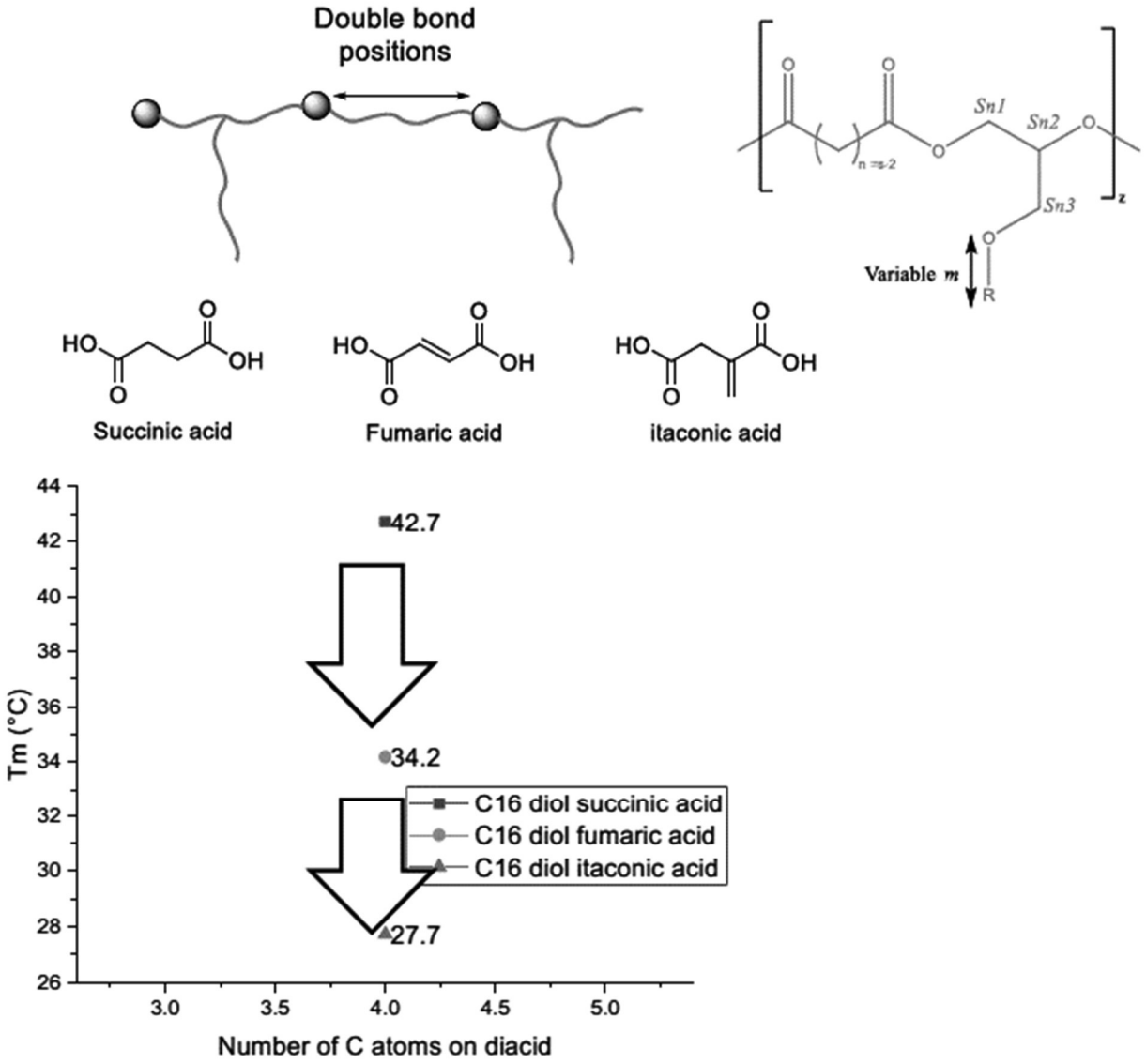
(c)


Pendent ether side chains
Polyester Backbone
Pendent ester side chains
Polyester Backbone

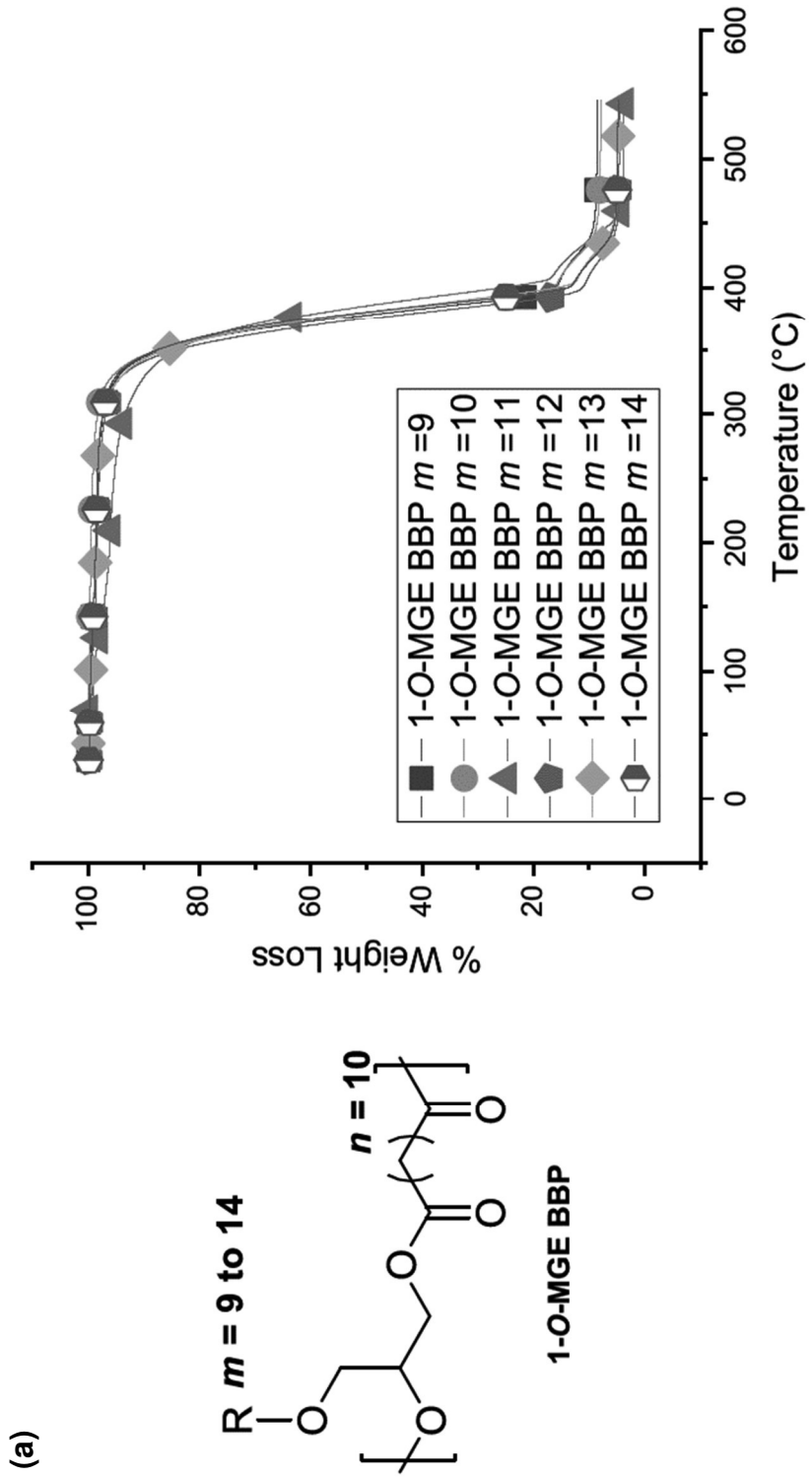
[Fig. 12]


R m = 18
varied n
n-2
2 carbons
Red circle: 1-O-MGE BBP
m = 18
R
varied n
n-2
3 carbons
Green square: 2-O-MGE BBP
1-O-MGE BBP, m=18
2-O-MGE BBP, m=18
30.8
33.4
28.3
30.0
31.9
22.8
21.9
17.9
17.9
20.0
14.9
11.6
T_m (°C)
n

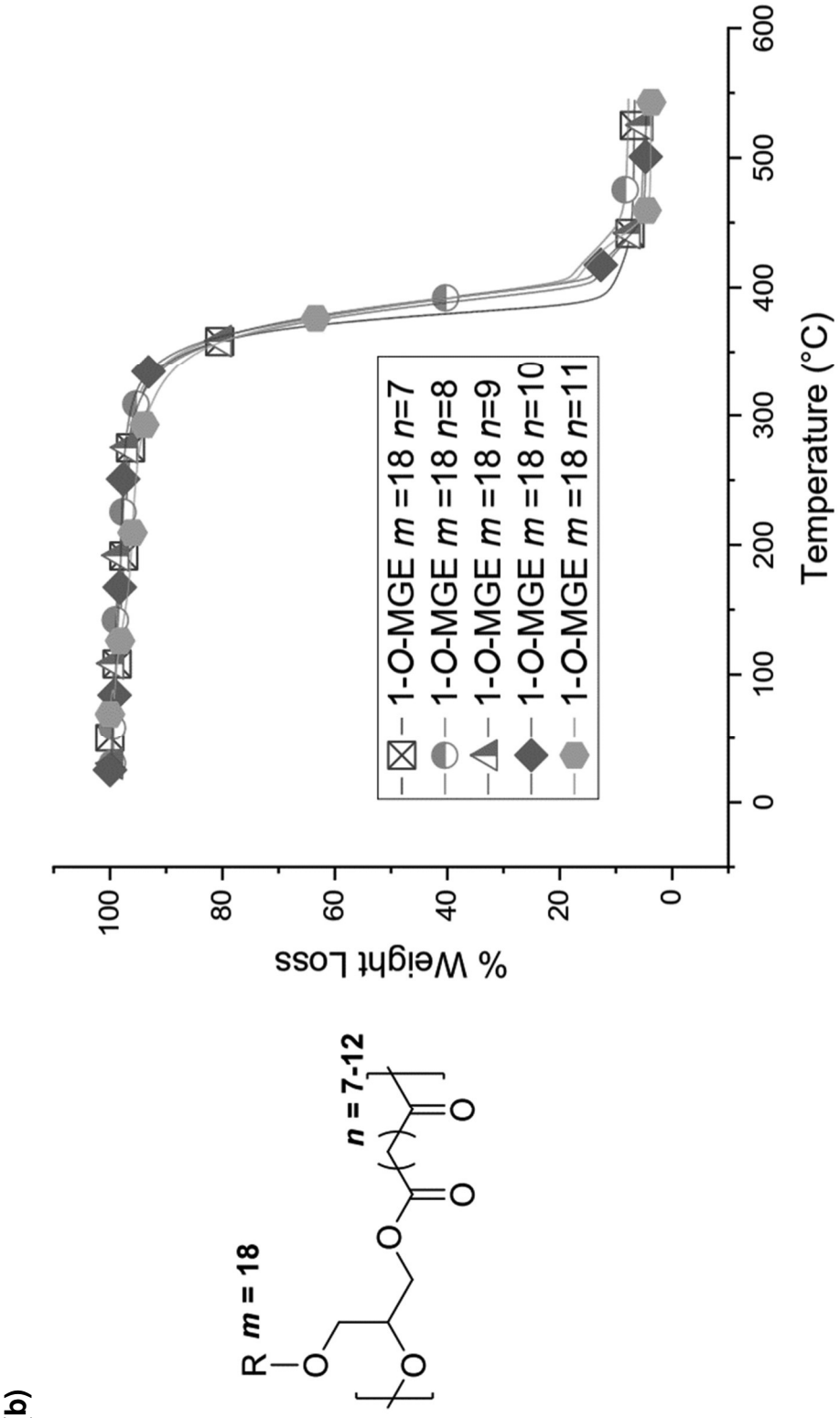
[Fig. 13]


Double bond positions
Sn1
Sn2
Sn3
Variable m
R
Succinic acid
Fumaric acid
itaconic acid
Tm (°C)
42.7
34.2
27.7
C16 diol succinic acid
C16 diol fumaric acid
C16 diol itaconic acid
Number of C atoms on diacid

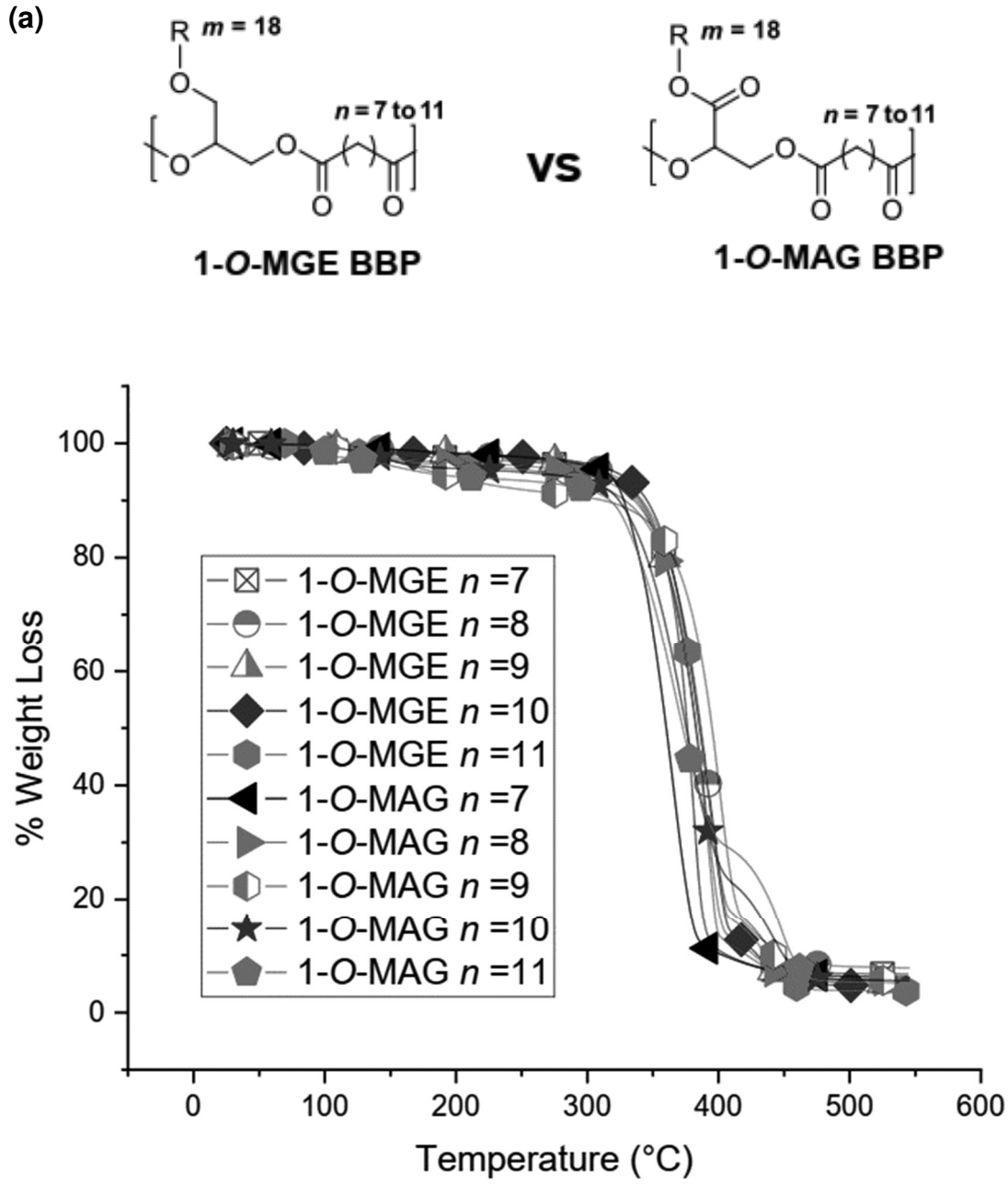
[Fig. 14]


(a)
R
m = 9 to 14
n = 10
1-O-MGE BBP
% Weight Loss
Temperature (°C)
1-O-MGE BBP m =9
1-O-MGE BBP m =10
1-O-MGE BBP m =11
1-O-MGE BBP m =12
1-O-MGE BBP m =13
1-O-MGE BBP m =14

[Fig. 14] cont.

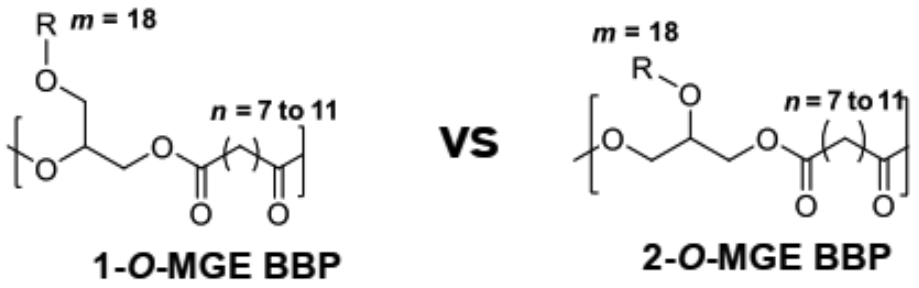

% Weight Loss
Temperature (°C)
1-O-MGE m =18 n=7
1-O-MGE m =18 n=8
1-O-MGE m =18 n=9
1-O-MGE m =18 n=10
1-O-MGE m =18 n=11
(b)
R—O
m = 18
n = 7-12

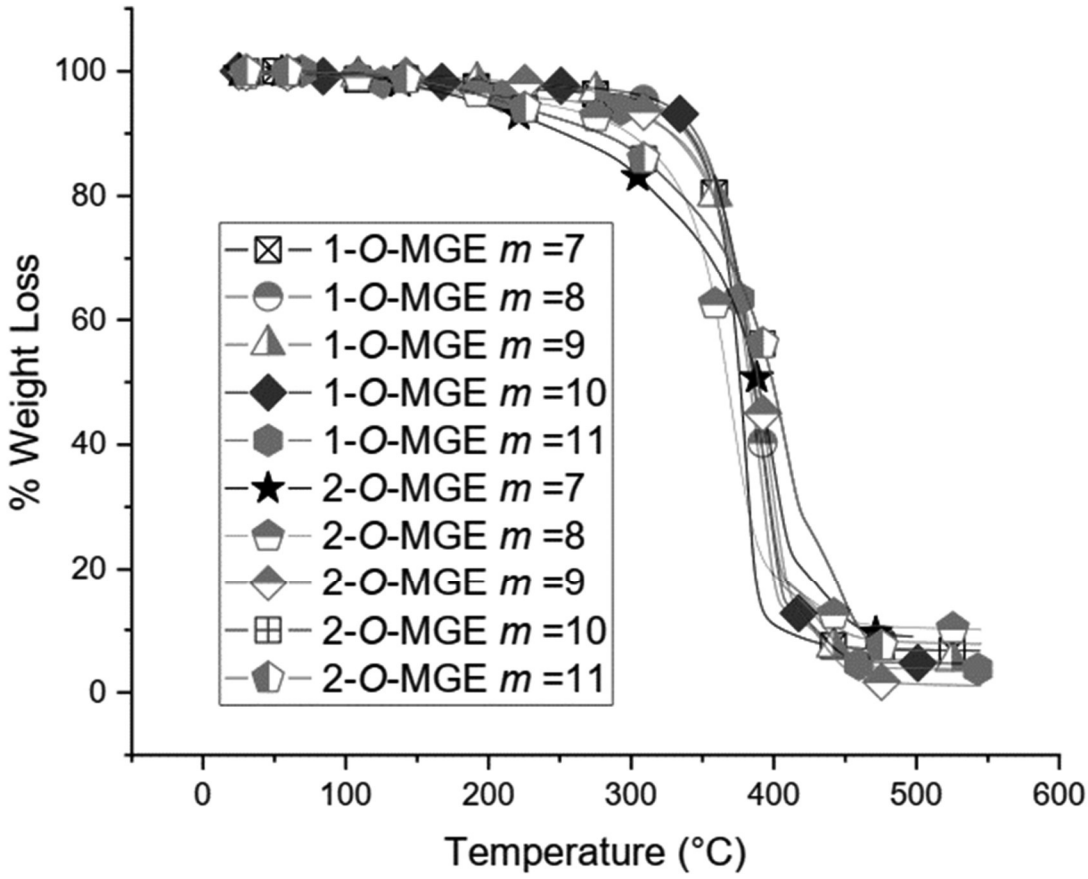
[Fig. 15]


(a)
R
m = 18
O
n = 7 to 11
O
O
O
O
VS
1-O-MGE BBP
1-O-MAG BBP
% Weight Loss
Temperature (°C)
0
20
40
60
80
100
0
100
200
300
400
500
600
1-O-MGE n =7
1-O-MGE n =8
1-O-MGE n =9
1-O-MGE n =10
1-O-MGE n =11
1-O-MAG n =7
1-O-MAG n =8
1-O-MAG n =9
1-O-MAG n =10
1-O-MAG n =11

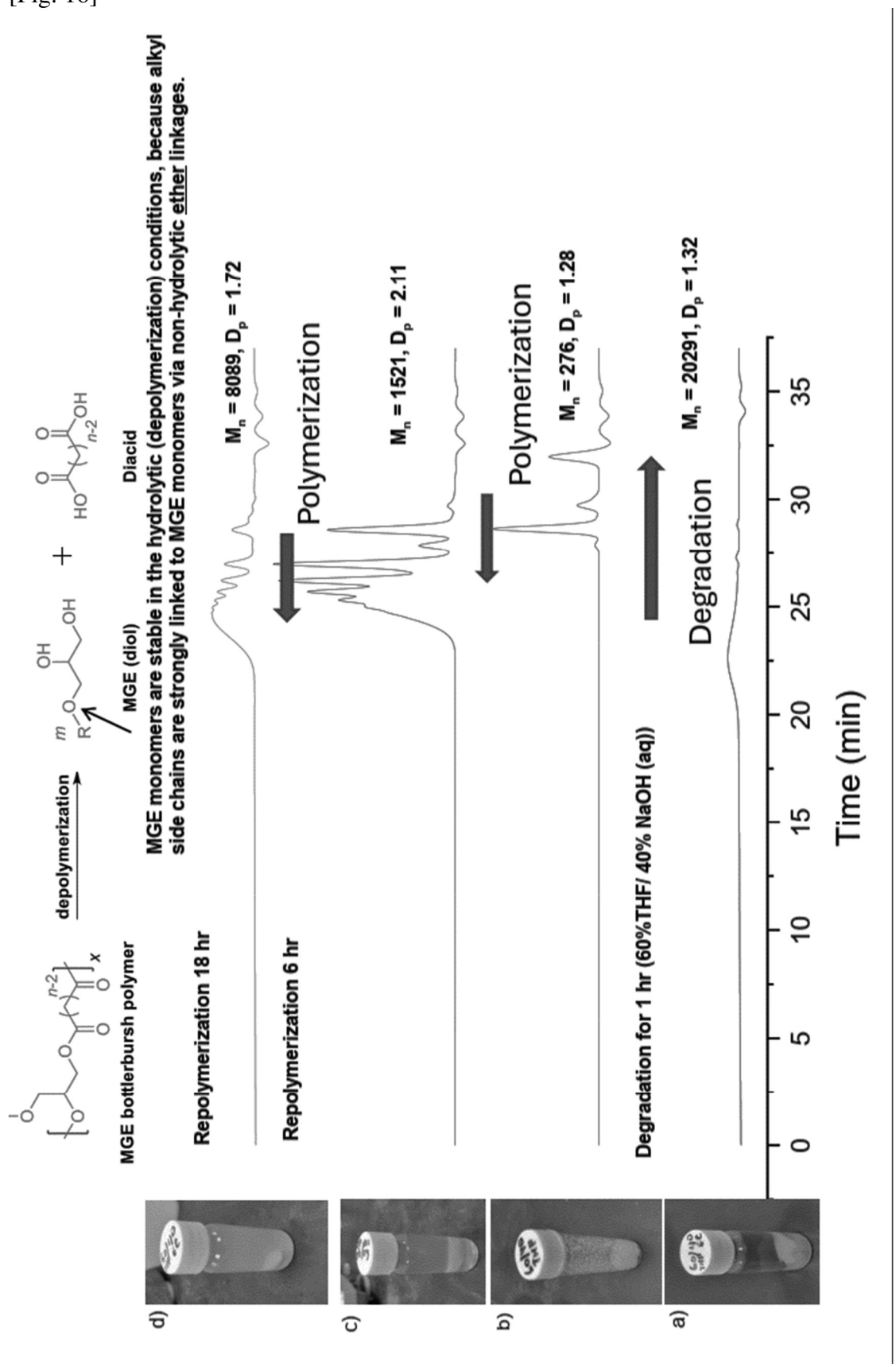
[Fig. 15] cont.

(b)

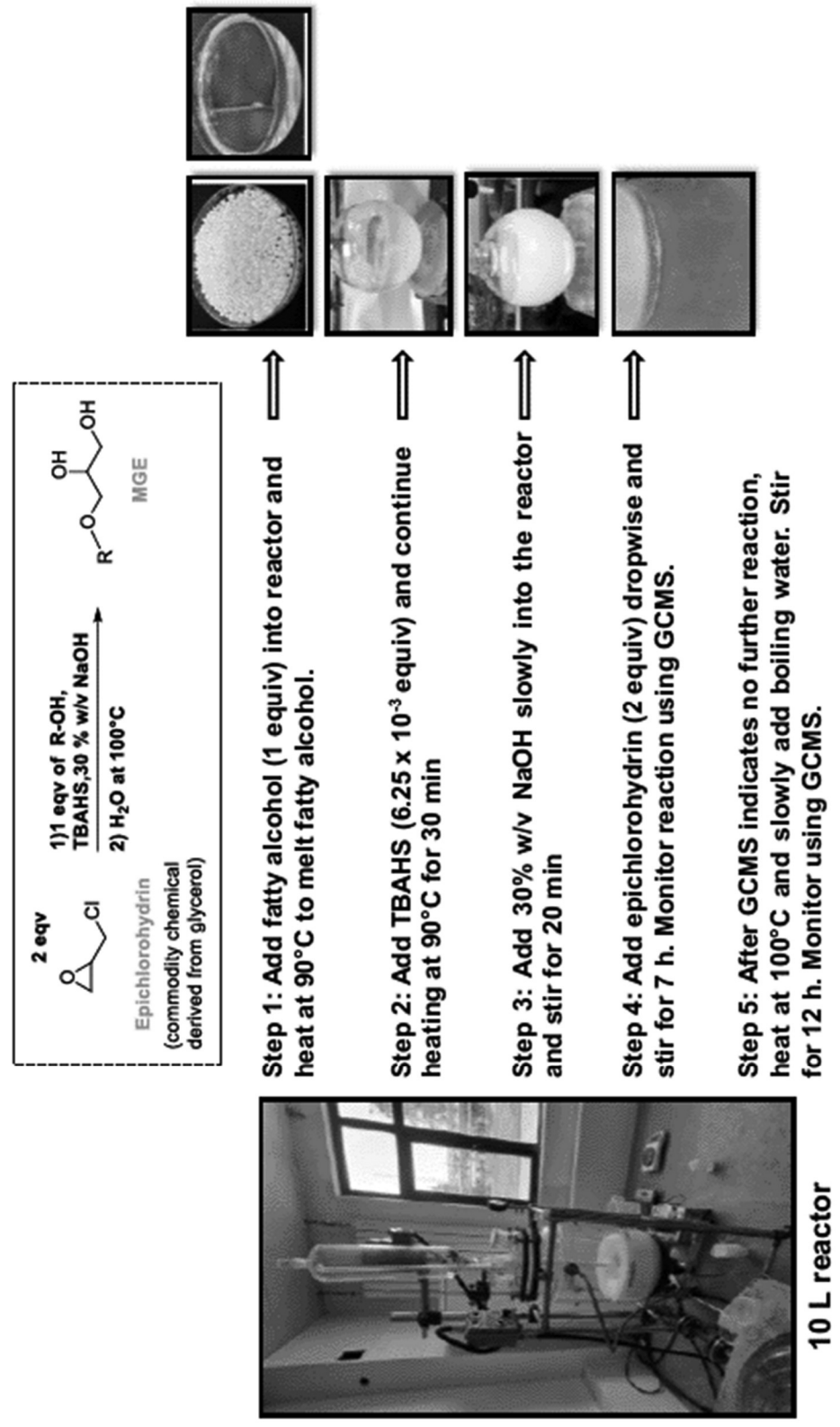

R
m = 18
O
n = 7 to 11
O
O
O
O
1-O-MGE BBP
VS
m = 18
R
O
n = 7 to 11
O
O
O
O
2-O-MGE BBP


% Weight Loss
Temperature (°C)
0
20
40
60
80
100
0
100
200
300
400
500
600
1-O-MGE m =7
1-O-MGE m =8
1-O-MGE m =9
1-O-MGE m =10
1-O-MGE m =11
2-O-MGE m =7
2-O-MGE m =8
2-O-MGE m =9
2-O-MGE m =10
2-O-MGE m =11

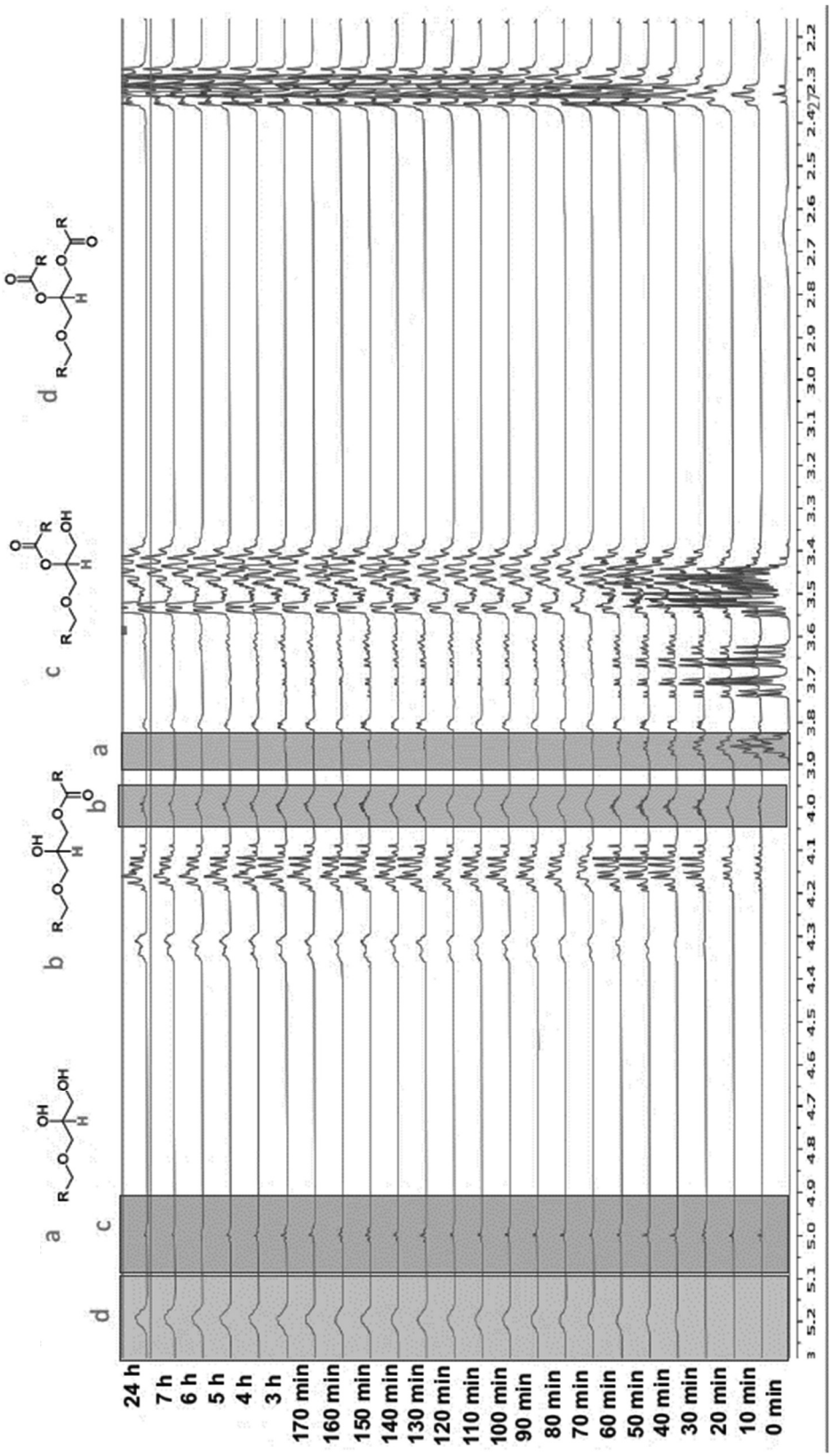
[Fig. 16]


MGE bottlerbursh polymer
depolymerization
MGE (diol)
Diacid
MGE monomers are stable in the hydrolytic (depolymerization) conditions, because alkyl side chains are strongly linked to MGE monomers via non-hydrolytic ether linkages.
Repolymerization 18 hr
Repolymerization 6 hr
Degradation for 1 hr (60%THF/ 40% NaOH (aq))
Polymerization
Polymerization
Degradation
Mn = 8089, Dp = 1.72
Mn = 1521, Dp = 2.11
Mn = 276, Dp = 1.28
Mn = 20291, Dp = 1.32
Time (min)
0
5
10
15
20
25
30
35
a)
b)
c)
d)

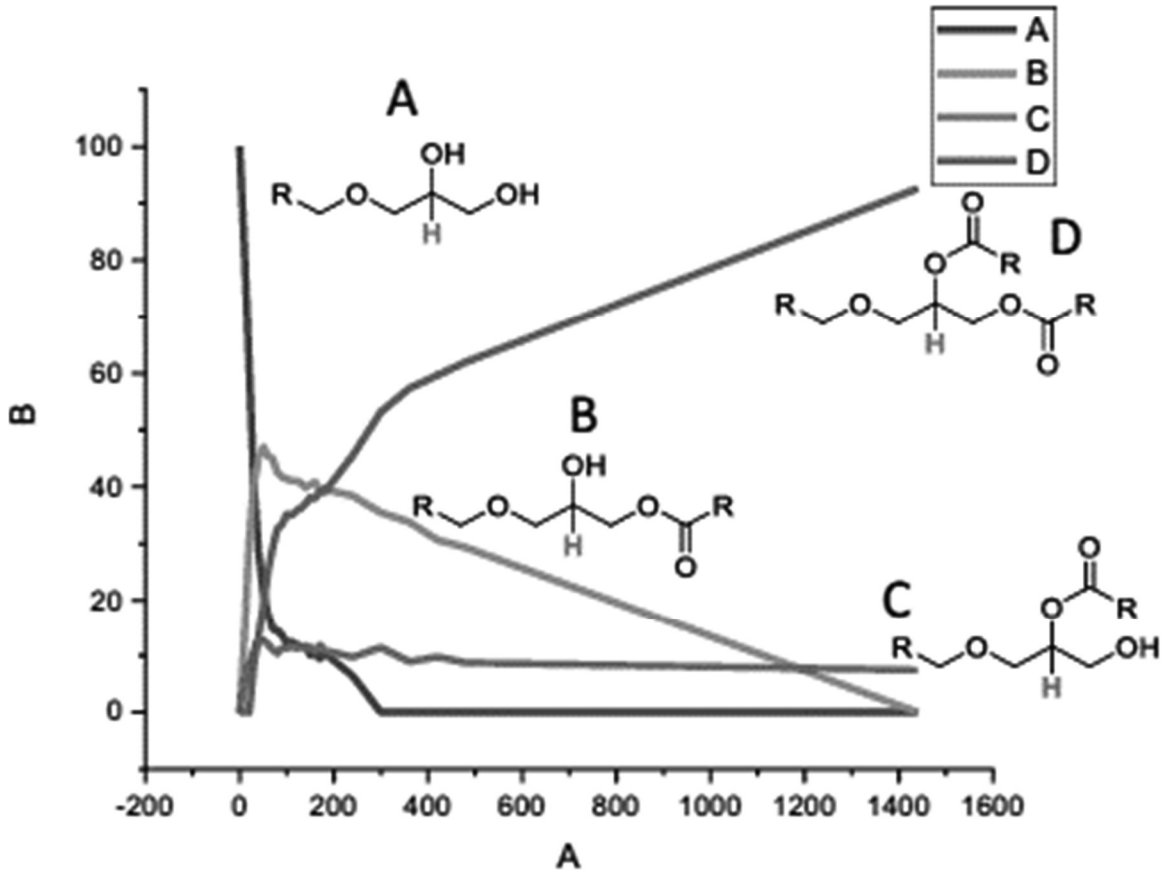
[Fig. 17]


2 eqv
1)1 eqv of R-OH, TBAHS,30 % w/v NaOH
2) H2O at 100°C
Epichlorohydrin
(commodity chemical derived from glycerol)
MGE
Step 1: Add fatty alcohol (1 equiv) into reactor and heat at 90°C to melt fatty alcohol.
Step 2: Add TBAHS (6.25 x 10-3 equiv) and continue heating at 90°C for 30 min
Step 3: Add 30% w/v NaOH slowly into the reactor and stir for 20 min
Step 4: Add epichlorohydrin (2 equiv) dropwise and stir for 7 h. Monitor reaction using GCMS.
Step 5: After GCMS indicates no further reaction, heat at 100°C and slowly add boiling water. Stir for 12 h. Monitor using GCMS.
10 L reactor

[Fig. 18]


24 h
7 h
6 h
5 h
4 h
3 h
170 min
160 min
150 min
140 min
130 min
120 min
110 min
100 min
90 min
80 min
70 min
60 min
50 min
40 min
30 min
20 min
10 min
0 min
a
b
c
d

[Fig. 19]


A
B
C
D
100
80
60
40
20
0
-200
0
200
400
600
800
1000
1200
1400
1600
A
B
OH
R
O
OH
H
O
R
O
R
O
R
O
H
O
R
O
R
O
O
R
O
R
O
OH
H