Synthesis and Amphiphilic Property of Substituted Acrylic Acid Polymer with Octadecyl Group

令和 6 年度
三重大学大学院　工学研究科
博士前期課程　分子素材工学専攻
高分子設計化学研究室

Syamim Syufiana Binti Sazali

Synthesis and Amphiphilic Property of Substituted Acrylic Acid Polymer with Octadecyl Group

Year 2024

Mie University Graduate School of Engineering

Department of Chemistry for Materials

Polymer Synthesis Laboratory

Syamim Syufiana Binti Sazali

Table of Content

Chapter 1 Introduction 4

Chapter 2 Experimental 12

2.1 Synthesis of α-substituted acrylic acids (5) 18

2.1.1 Synthesis of *tert*-Butyl 2-(Hydroxymethyl)acrylate (**2**) 18

2.1.2 Synthesis of *tert*-Butyl 2-(Bromomethyl)acrylate (**3**) 19

2.1.3 Synthesis of *tert*-Butyl 2-(Octadecyloxymethyl)acrylate (**4**) 20

2.1.4 Synthesis of 2-(Octadecyloxymethyl)acrylic acid (**5**) 21

2.2 Synthesis of atactic polymer (Poly 3) 22

2.2.1 Synthesis of Poly(2-(Octadecyloxymethyl)acrylic acid) (**Poly-3**) 22

2.3 List of solvents 23

2.4 List of reagents 24

2.5 List of equipment 25

Chapter 3 Results and Discussion 38

3.1 Radical Polymerization of 2-(Octadecyloxymethyl)acrylic acid (5) 39

3.2 Evaluation of Amphiphilicity of Poly(2-(Octadecyloxymethyl)acrylic acid) (Poly-3) 41

3.2.1 Calibration curve for Rhodamine B 41

3.2.2 Extraction experiment of Rhodamine B 43

3.3 Effect of Molecular Structure on Extractability 45

3.3.1 Poly(2-(Dodecyloxymethyl)acrylic acid) (**Poly-2**) and Poly(2-(Octadecyloxymethyl)acrylic acid) (**Poly-3**) 45

Chapter 4 Conclusion 48

References 50

Acknowledgment 51

CHAPTER 1 Introduction

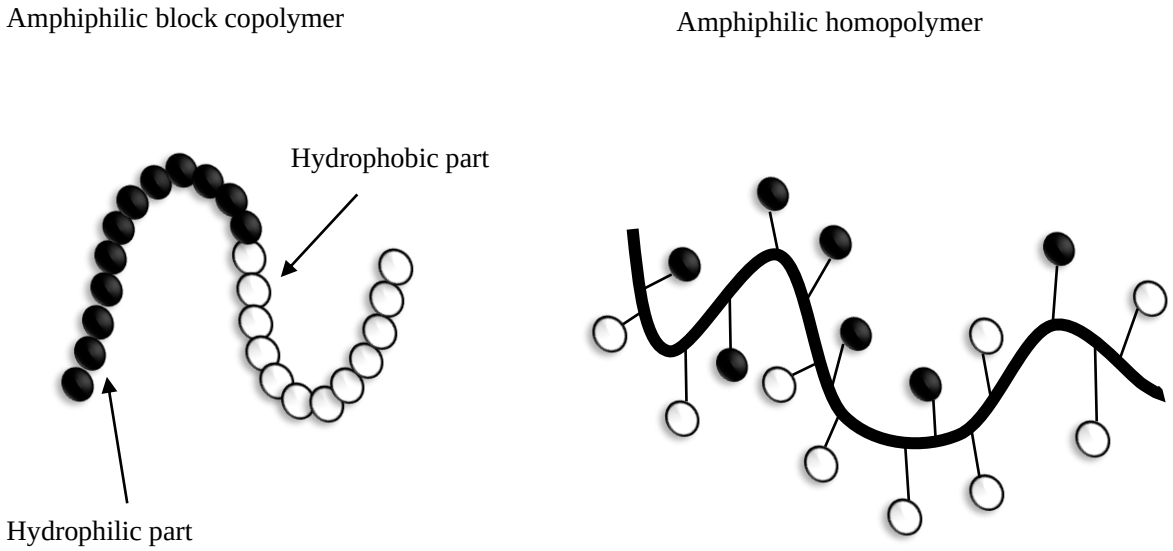
Amphiphilic polymers are a fascinating and versatile class of macromolecules that exhibit unique characteristics due to their dual nature. Controlling the self-assembly of amphiphilic polymers in water is crucial for creating polymer materials with precise three-dimensional structures and desirable properties. Because it is triggered by the association of the hydrophobic segments in water, the self-assembly of amphiphilic polymers depends on the primary structure: the composition (hydrophobic and hydrophilic parts), sequence distribution (layout), and structural and physical properties (bulkiness, density, crystallinity, etc.) of the built-in monomer units, in addition to the degree of polymerization (DP, chain length) of the polymers.[1]

One of the most remarkable behaviors of amphiphilic polymers is their ability to self-assemble into various nanostructures, such as micelles, vesicles, and bilayers, depending on the specific conditions and the polymer's composition. For instance, micelles are spherical structures with a hydrophobic core and a hydrophilic shell, which can encapsulate hydrophobic molecules, making them ideal for drug delivery applications. Conversely, vesicles are hollow spheres with an aqueous interior, surrounded by a bilayer of amphiphilic polymers, suitable for carrying both hydrophilic and hydrophobic substances.[2,3]

One method of synthesizing amphiphilic polymers is to synthesize amphiphilic block copolymers by linking hydrophilic and hydrophobic polymer chains. The structure is regulated by the balance of hydrophobic interactions and the interaction between the solvent and hydrophilic part, and various forms can be constructed, including micellar and lamellar structures. However, in general, the synthesis of amphiphilic block copolymers requires precision synthesis techniques such as living polymerization methods and cannot be easily

obtained.[4] On the other hand, it is possible to synthesize amphiphilic polymers by polymerization of amphiphilic monomers in which hydrophilic and hydrophobic groups are introduced into one molecule, which is relatively easier than the synthesis of amphiphilic block copolymers and is considered advantageous for achieving both hydrophilic and hydrophobic properties.

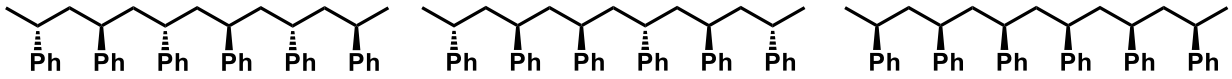
Amphiphilic polymer



For example, the substituent group in a polymer can be a methyl group in polypropylene, a chlorine atom in poly(vinyl chloride), or a phenyl ring in polystyrene. The polymer is termed isotactic when all the R groups are aligned on the same side of the plane formed by the extended-chain backbone. If the substituent groups alternate regularly from one side of the plane to the other, the polymer is known as syndiotactic. Polymers with no specific arrangement of substituent groups are referred to as atactic. Although more complex configurations of

substituent groups can occur in 1,2-disubstituted polymers, these are less commercially significant and will not be covered here. Generally, tactic polymers (isotactic or syndiotactic) are partially crystalline, while atactic polymers are amorphous, lacking any crystalline order. Tacticity also significantly influences other polymer properties, such as thermal and mechanical behavior. Whether a polymer becomes atactic, isotactic, or syndiotactic depends on specific polymerization conditions, such as temperature and solvent choice.[5]

Syndiotactic Polystyrene Atactic Polystyrene Isotactic



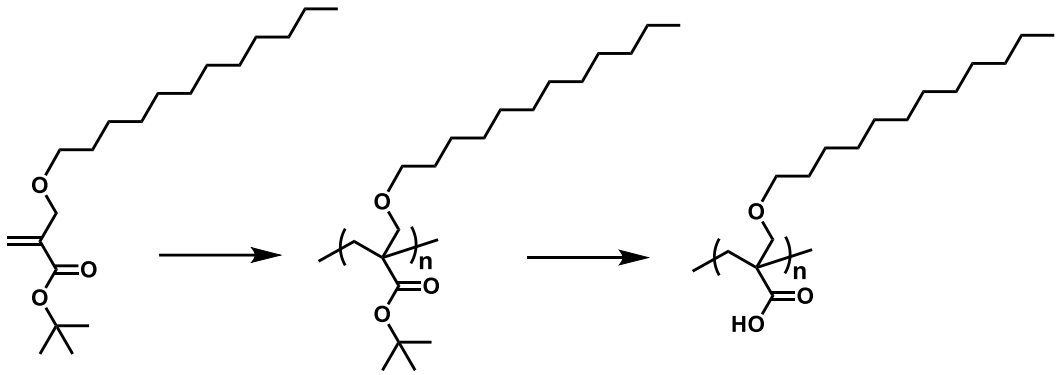
Polystyrene

Melting point: 270°C Amorphous, no melting point Melting point: 240°C

The method of polymerization influences the tacticity of the resulting polymer. Radical polymerization generally produces atactic polymers due to the random nature of the free radical mechanism. In contrast, coordination polymerization methods, such as those using Ziegler-Natta or metallocene catalysts, can produce isotactic or syndiotactic polymers by controlling the orientation of monomer units during polymerization.

In past research, we investigated the polymerization reactivity of amphiphilic α-substituted acrylic esters (**1**) having a dodecyloxy group as a hydrophobic group and the stereoregularity of the generated polymers. Subsequently, the ester moiety of the product polymer was converted

to a carboxy group by thermal decomposition, and a stereo-regular polymer (**Poly-1**) was synthesized.

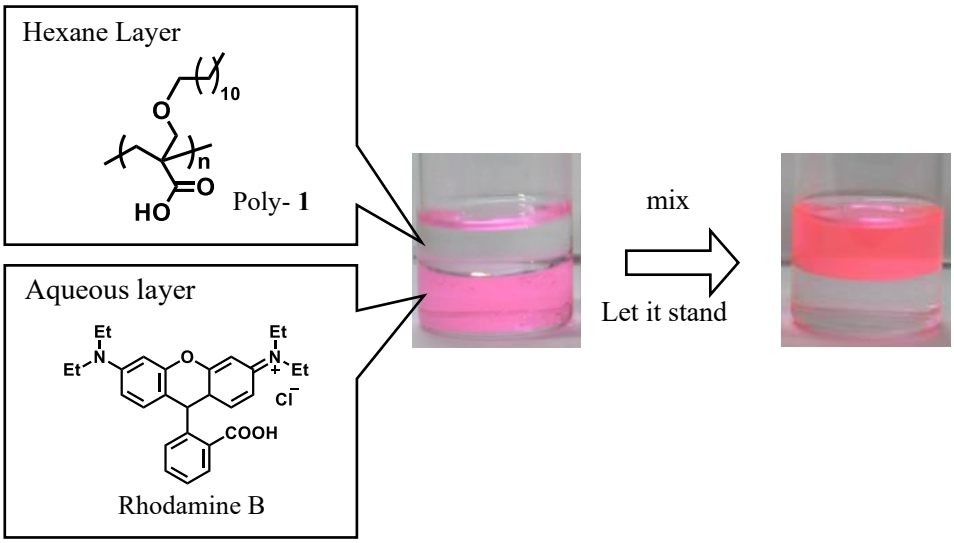


1 **Poly-1**

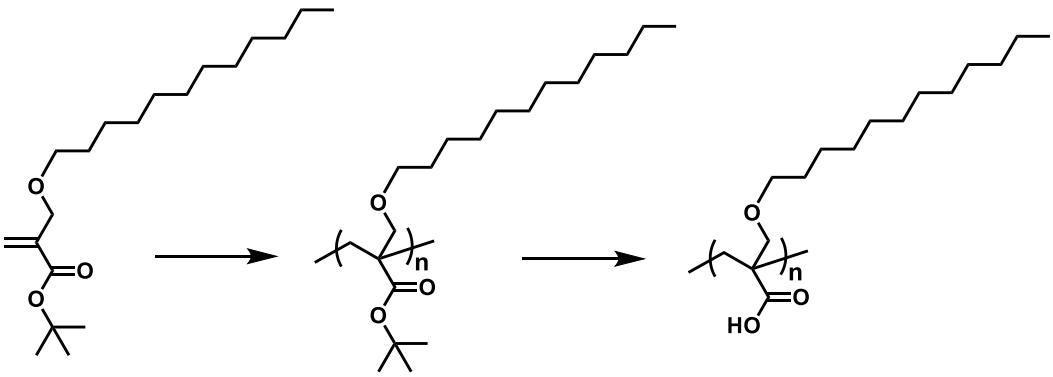
Despite being a polycarboxylic acid, **Poly-1** is insoluble in water and methanol, and soluble in a wide range of organic solvents from low to high polarity, especially in non-polar solvents such as hexane, indicating that it forms reverse micelles with a carboxy group as the core and a dodecyl group as the shell. When a hexane solution of **Poly-1** (colorless) and an aqueous solution of Rhodamine B (pink) were mixed and allowed to stand, the pink color of the aqueous layer faded and the hexane layer became pink in color. This is thought to be because the Rhodamine B solution was extracted into the hexane layer by being encapsulated in the core of reverse micelles formed by **Poly-1** in hexane as microdroplets, indicating that **Poly-1** exhibits reverse micellar extractability.

Furthermore, the effect of stereoregularity on the reverse micellar extractability was investigated, and the atactic **Poly-1** showed higher extractability than the isotactic **Poly-1**, indicating that stereoregularity affects the amphiphilic properties of polymers. However, when

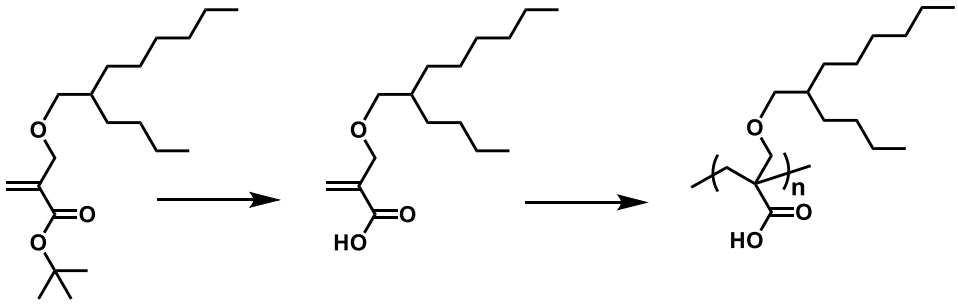
the particle size distribution of **Poly-1** was measured in hexane, a component with a small particle size of a few nm, corresponding to an inverse micelle formed by a single polymer chain (unimolecular micelle), and a component with a larger particle size of about 250 nm were observed. This larger particle size is larger than the mesh size (100 m) of the filter used to filter the sample solution during sample preparation, suggesting that reverse micelles form aggregates with each other in solution.[6]



In other recent research, the investigation of branched hydrophobic groups into amphiphilic poly(α-substituted acrylic acid) was started. A new α-substituted acrylic acid monomer (**2**) in which a branched dodecyl group, 2-butyloctyl group, introduced instead of a linear dodecyl group was synthesized and polymerized. The amphiphilic properties of **Poly-2** and **Poly-1** were compared, and the effects of hydrophobic substituent structure, molecular weight, and temperature on the amphiphilic properties were investigated.



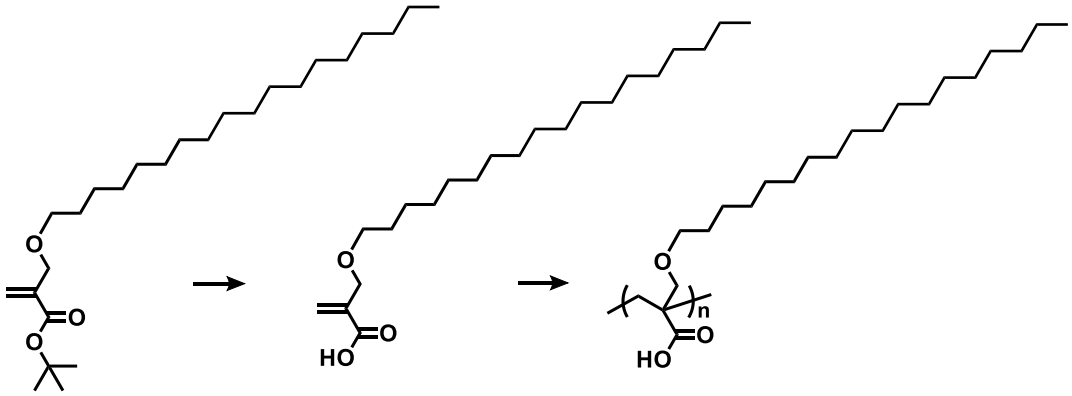
1 **Poly-1**



2 **Poly-2**

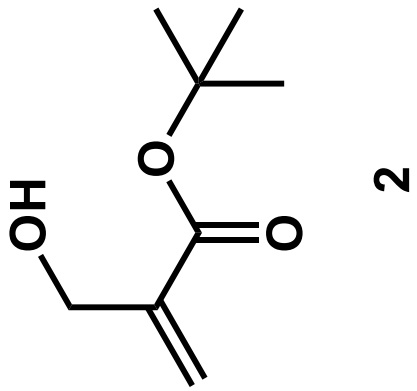
The results of the investigation showed that there was no effect of molecular weight on the thermal properties of the structure. This may be attributed to the amorphous nature of the branched side chain structure. However, the temperature may have some effects. For low molecular weight materials, the extraction rate did not change with temperature, but as the molecular weight increased, the extraction rate changed. The increase or decrease depended on the molecular weight, suggesting that the extraction rate was temperature-dependent. Furthermore, the absorbance of the hexane layer increased when the sample was cooled after the temperature was raised, suggesting that the change in extraction rate with temperature is reversible. However, it was impossible to fully discuss which of the two polymers, **Poly-1**, and **Poly-2**, was more temperature-dependent from the extraction experiment alone.

In this work, we aim to investigate a novel amphiphilic homopolymer (**Polyw-3**) with a longer octadecyl group instead of a dodecyl group as a hydrophobic group and investigate the effect of hydrophobic alkyl chain length on those amphiphilic properties.



Poly-3

CHAPTER 2 Experimental



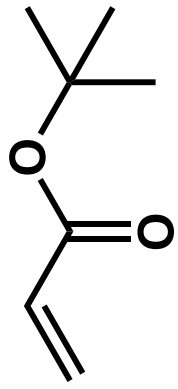
2

DABCO

1,4-dioxane/H_2O

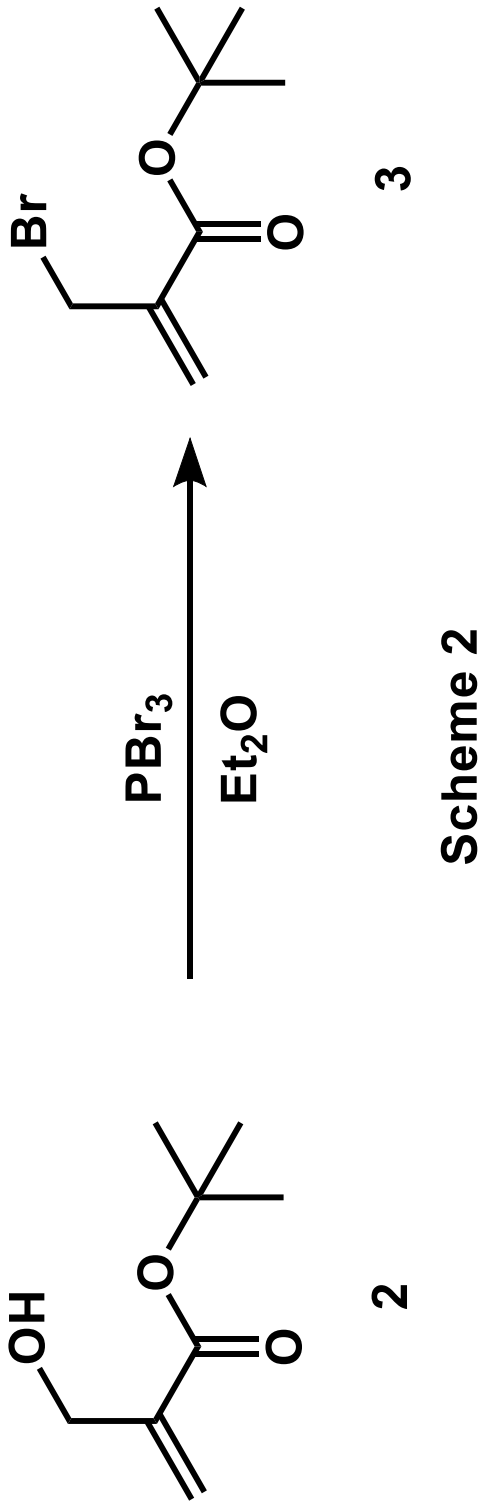
HCHO

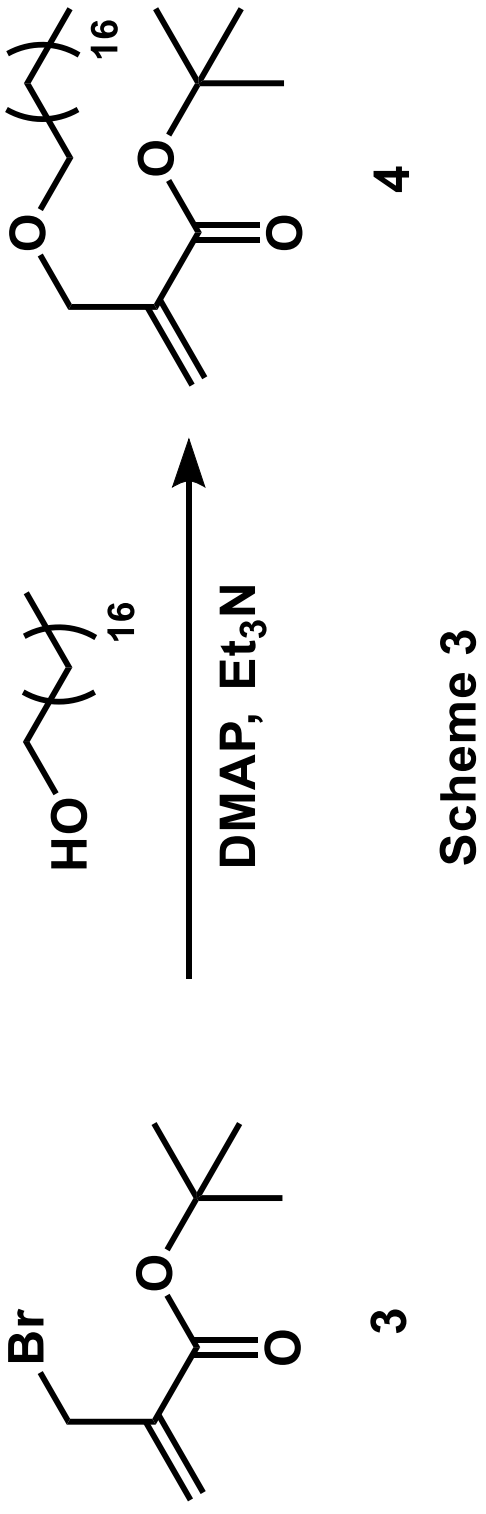
+



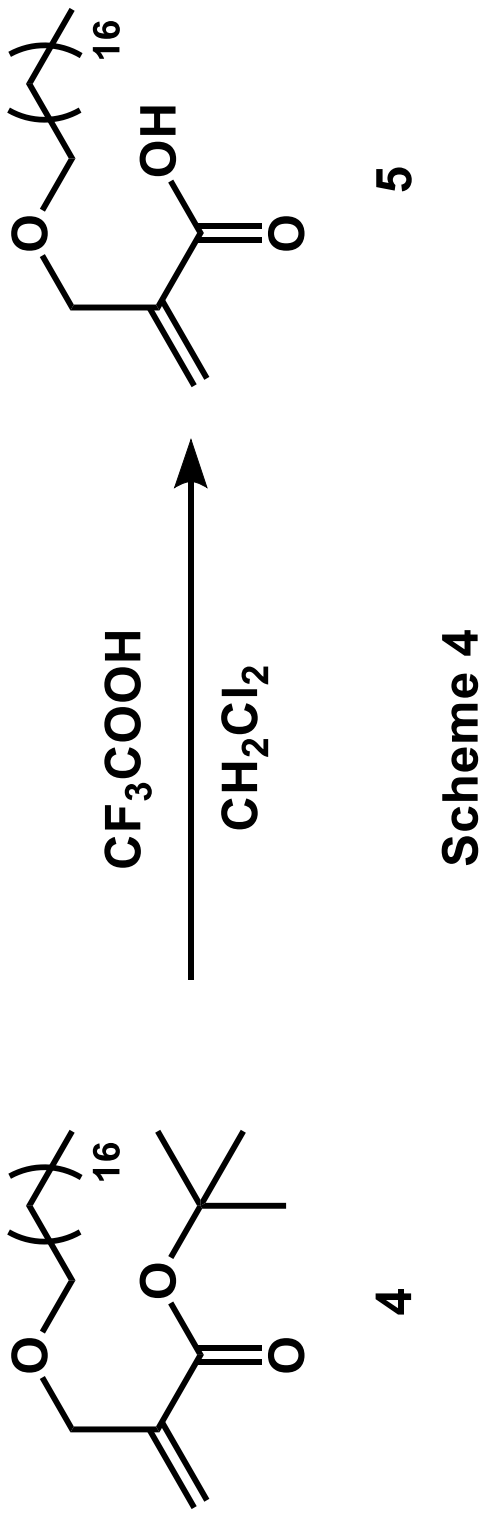
1

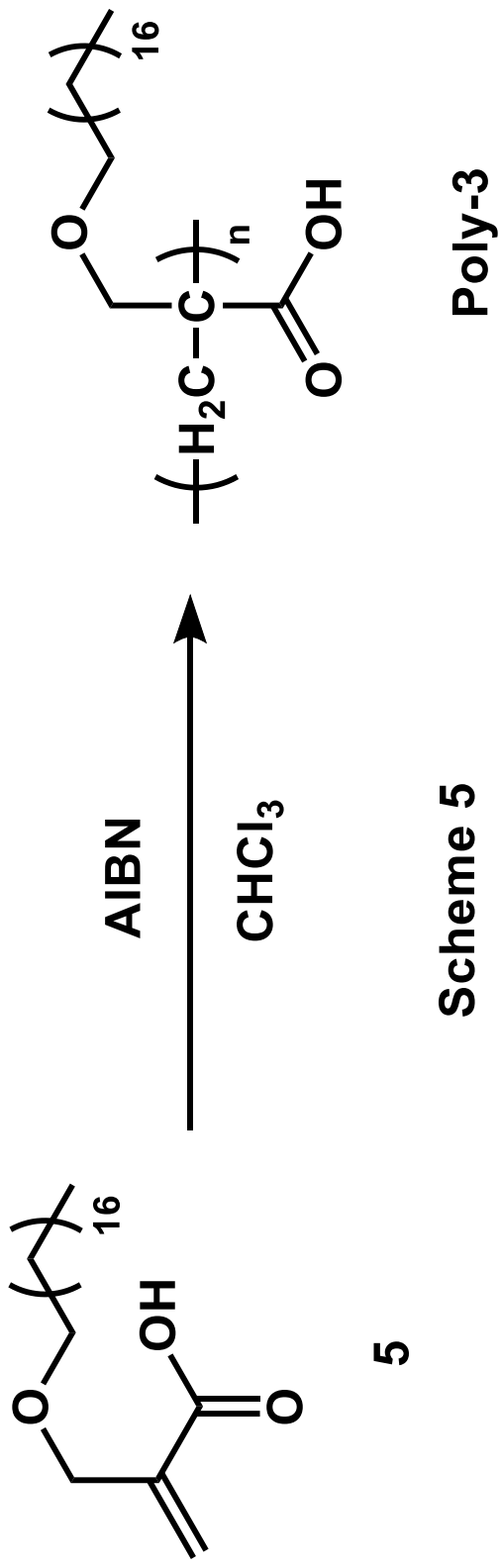
Scheme 1


Br
O
O
3
PBr3
Et2O
Scheme 2
OH
O
O
2



Scheme 3


16
OH
O
O
5
CF3COOH
CH2Cl2
Scheme 4
16
O
O
O
O
4



Poly-3

Scheme 5

5

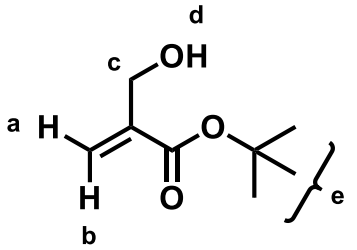
2.1 Synthesis of α-substituted acrylic acids (5)

2.1.1 Synthesis of *tert*-Butyl 2-(Hydroxymethyl)acrylate (**2**) (Scheme 1)

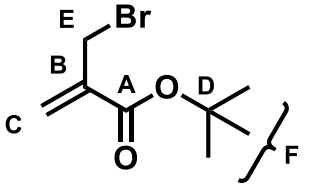
In a 1000 ml round-bottom flask, *tert*-Butyl Acrylate ($C_7H_{12}O_2$) (**1**) 20.0 g (156 mmol), 1,4-Diazabicyclo[2.2.2]octane (DABCO) 17.5 g (156 mmol), 1,4-Dioxane 200 ml, Formaldehyde (HCHO)12.7 g (156 mmol) and 200 ml of distilled water (H_2O) were weighed and stirred on a magnetic stirrer at room temperature for 48 hours. After completing the process, the solution was poured into a separating funnel to be extracted with Diethyl Ether and washed with distilled water. The ether solution was mixed with anhydrous Magnesium Sulfate to remove any water molecules. The solution was evaporated under reduced pressure. The silica gel column (chloroform) procedure was performed to separate the foreign component from the solution. The *tert*-Butyl 2-(Hydroxymethyl)acrylate (**2**) was successfully obtained as a clear colorless liquid.

Yield 5.71 g (23.1%)

- ^{1}H NMR ($CDCl_3$), δ, ppm (Fig 1)
  a) 6.13 (s, 1H) b) 5.72 (s, 1H)
  c) 4.27 (d, 2H) d) 2.42 (t, 1H)
  e) 1.50 (s, 9H)



- ^{13}C NMR ($CDCl_3$), δ, ppm (Fig 2)
  A) 165.8 B) 140.9
  C) 124.8 D) 81.5
  E) 62.8 F) 28.1



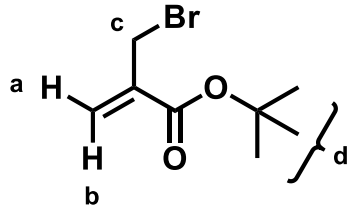
- IR (NaCl), cm^{-1} (Fig 3)
  3427 (ν_{O-H}) 2934 (ν_{C-H}) 1708 ($\nu_{C=O}$) 1152 (ν_{C-O})

2.1.2 Synthesis of *tert*-Butyl 2-(Bromomethyl)acrylate (**3**) (Scheme 2)

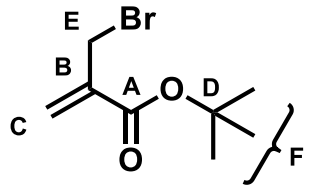
In a 200 ml round-bottom flask, 5.71 g (36.09 mmol) of *tert*-Butyl 2-(Hydroxymethyl)acrylate (**2**) and 49 ml of Diethyl Ether were weighed and stirred on a magnetic stirrer. The reaction system was cooled to -10 ºC, and then 4.87 g (18 mmol) of Phosphorus Tribromide was added and stirred under nitrogen for 6 hours. After completion, saturated sodium bicarbonate solution was added to the reaction mixture to make it basic. The solution was then transferred into a separating funnel, extracted with Diethyl Ether, and washed with distilled water. After drying with anhydrous Magnesium Sulfate, the solvent was removed under reduced pressure to afford *tert*-Butyl 2-(Bromomethyl)acrylate (**3**) as a clear colorless liquid.

Yield 4.56 g (57.1%)

- ^{1}H NMR ($CDCl_3$), δ, ppm (Fig 4)
  a) 6.21 (s, 1H) b) 5.84 (s, 1H)
  c) 4.13 (d, 2H) d) 1.51 (s, 9H)



- ^{13}C NMR ($CDCl_3$), δ, ppm (Fig 5)
  A) 164.1 B) 139.0
  C) 128.0 D) 81.8
  E) 29.9 F) 28.1



- IR (NaCl), cm^{-1} (Fig 6)
  2978 (ν_{C-H}) 1719 ($\nu_{C=O}$) 1369 (ω_{CH_2}) 1156 (ν_{C-O})

2.1.3 Synthesis of *tert*-Butyl 2-(Octadecyloxymethyl)acrylate (**4**) (Scheme 3)

3.00 g (13.6 mmol) of *tert*-Butyl 2-(Bromomethyl)acrylate (**3**), 11.3 ml of Dichloromethane (CH_2Cl_2), 5.5 g (20.3 mmol) of 1-Octadecanol, 0.17 g (1.39) of DMAP, and 4.13 g (40.81 mmol) of Triethylamine (Et_3N) were weighed and mixed in an round-botttom flask. The solution mixture was stirred in an oil bath with reflux under nitrogen for 7 days. After completion of the reaction, 1N HCl aq was added to make it acidic. The separation liquid process was performed using CH_2Cl_2 and washed with saturated brine. After drying with anhydrous Magnesium Sulfate, the solvent was removed under reduced pressure and the first component was separated by silica gel column (chloroform) to obtain *tert*-Butyl 2-(Octadecyloxymethyl)acrylate (**4**) as a clear colorless liquid..

Yield 1.74 g (31.13%)

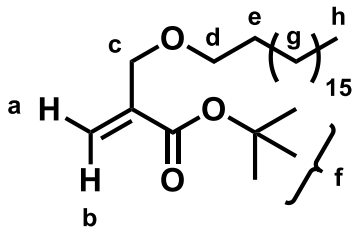
- ^{1}H NMR ($CDCl_3$), δ, ppm (Fig 7)

  a) 6.19 (s, 1H) b) 5.78 (s, 1H)

  c) 4.14 (s, 1H) d) 3.48 (t, *J* = 6.0 Hz, 2H)

  e) 1.60 (br, 2H) f) 1.50 (s, 9H)

  g) 1.26 (br, 30H) h) 0.88 (t, *J* = 6.0 Hz, 3H)



2.1.4 Synthesis of 2-(Octadecyloxymethyl)acrylic Acid (**5**) (Scheme 4)

In a 100 ml round-bottom flask equipped with a magnetic stirrer, 1.28 g of *tert*-butyl 2-(Octadecyloxymethyl)acrylate (**4**), 1.28 g of Trifluoroacetic acid (CF_3COOH) and 15 ml of Dichloromethane (CH_2Cl_2) were added. The mixture was stirred at room temperature for 24 hours. After completion, 1N HCl aq was added and extracted with Ddichloromethane. After drying with anhydrous Magnesium Sulfate, the solvent was removed under reduced pressure to afford 2-(Octadecyloxymethyl)acrylic Acid (**5**) as a colorless solid.

Yield 0.118 g (91%)

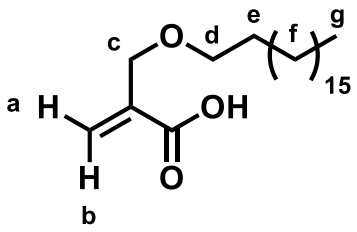
- ^{1}H NMR ($CDCl_3$), δ, ppm (Fig 8)

  a) 6.19 (s, 1H) b) 5.78 (s, 1H)

  c) 4.14 (s, 1H) d) 3.48 (t, J = 6.0 Hz, 2H)

  e) 1.60 (br, 2H) f) 1.50 (s, 9H)

  g) 1.26 (br, 30H) h) 0.88 (t, J = 6.0 Hz, 3H)



- ^{13}C NMR ($CDCl_3$), δ, ppm (Fig 9)

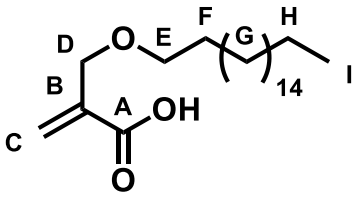
  A) 170.4 B) 136.7

  C) 128.1 D) 71.3

  E) 68.7 F) 32.0

  G) 29.7 H) 22.8

  I) 14.2



- IR ($CDCl_3$), cm^{-1}(Fig 10)

  2400 ~ 3500 (ν_{O-H}) 2914 (ν_{C-H}) 1697 ($\nu_{C=O}$) 1125 (ν_{C-O})

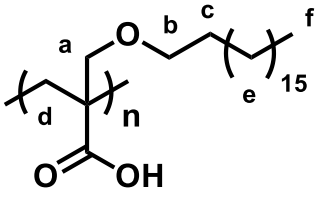
2.2 Synthesis of atactic polymer (Poly-3)

2.2.1 Synthesis of Poly(2-(octadecyloxymethyl)acrylic acid) (**Poly-3**) (Scheme 5)

200 mg (0.564 mmol) of monomer (**5**), 1.853 mg of 2,2'-Azobis(isobutyronitrile) (AIBN) as initiator were weighted into an ampoule tube and 1.5 ml of purified chloroform was added under nitrogen. The ampoule tube was then degassed 3 times by freeze-thaw method. The reaction was carried out at 60 ^{o}C for 48 hours, and the white solid polymer (**Poly-3**) was isolated by re-precipitation with methanol and hexane.

Yield 0.1653 g (82.7%)

GPC: Mn = 7,900, Mw/Mn = 2.19



- ^{1}H NMR ($CDCl_3$), δ, ppm (Fig 11)
  a, b) 3.3 (br, 4H) c, d) 1.9 (br, 4H)
  e) 1.2 (br, 30H) f) 0.9 (br, *3*H)
- IR ($CDCl_3$), cm^{-1}(Fig 12)
  3500 ~ 2500 (ν_{O-H}) 2851 (ν_{C-H}) 1719 ($\nu_{C=O}$) 1114 (ν_{C-O})

2.3 List of solvents

- Purified chloroform

The solvents listed below were used as they are commercially available.

- Chloroform ($CHCl_3$)
- Dichloromethane (CH_2Cl_2)
- Diethyl Ether (Et_2O)
- Methanol (MeOH)
- Hexane
- 1,4-Dioxane
- Ethyl Acetate ($C_4H_8O_2$)

2.4 List of reagents

The reagents listed below were used as they are commercially available.

- *tert*-butyl Acrylate
- 1,4-Diazabicyclo[2.2.2]octane (DABCO)
- Formaldehyde (37%) (HCHO)
- Phosphorus Tribromide (PBr_3)
- Sodium Bicarbonate ($NaHCO_3$)
- Anhydrous Magnesium Sulfate ($MgSO_4$)
- Dichloromethane (CH_2Cl_2)
- 4-Dimethylaminopyridine (DMAP)
- Triethylamine (Et_3N)
- 1-Octadecanol
- Hydrochloric Acid (HCl)
- Sodium Chloride (NaCl)
- Trifluoroacetic Acid (CF_3COOH)
- 2,2'-Azobis(isobutyronitrile) (AIBN)
- Silica gel
- Rhodamine B

2.5 List of equipment

- ^{1}H NMR, ^{13}C NMR spectroscopy
  JEOL JNM-A500 type　High-resolution nuclear magnetic resonance spectrometer

- IR spectrometer
  JASCO FT/IR-4100 type　Infrared spectrometer

- GPC measurement
  (for polymer) Pump: JASCO　PU-1580

  Detector: JASCO　RI-930

  Column: TOSOH　TSKgel　MultiporeH_{XL}-M×2

  Eluent: THF

  Standard: Polystyrene

- Centrifuge

  KUBOTA Table Top Multi-Stack Centrifuge 8420

- UV-Vis Measurement
  SHIMADZU UV-2550 type　UV visible spectrophotometer

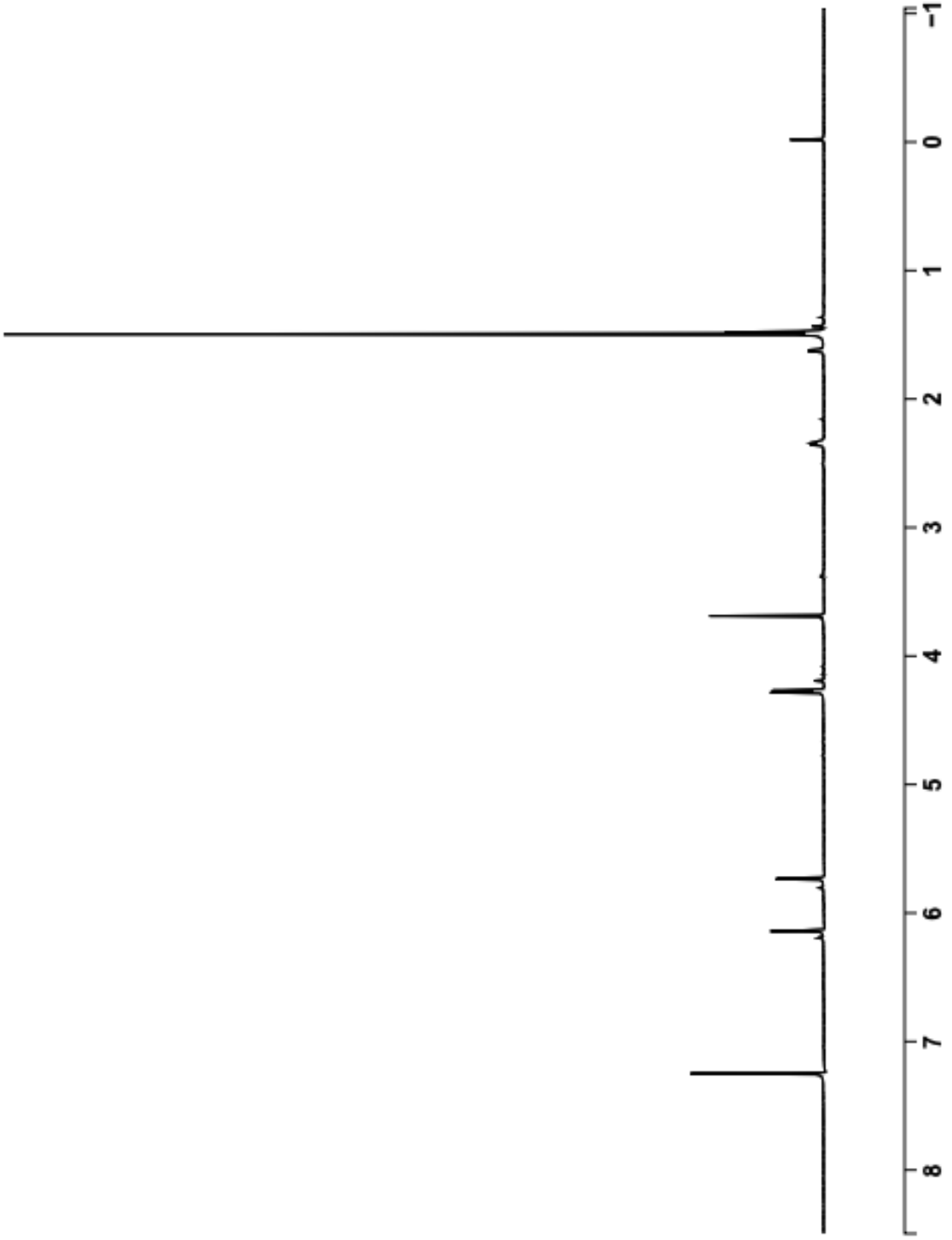


Fig. 1 ^{1}H NMR spectrum of *tert*-Butyl 2-(Hydroxymethyl)acrylate (**2**) ($CDCl_3$)

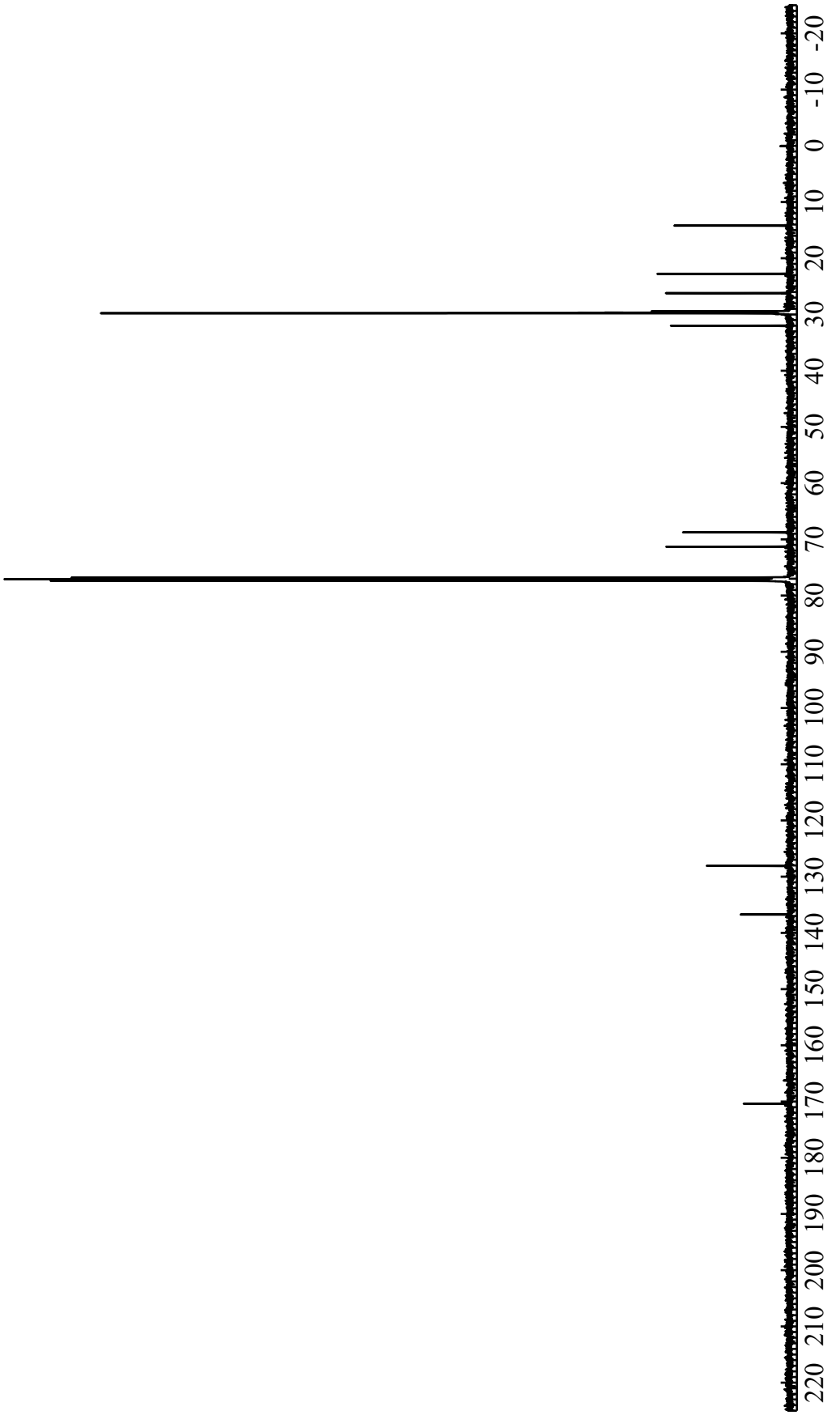


Fig. 2 ^{13}C NMR spectrum of *tert*-Butyl 2-(Hydroxymethyl)acrylate (**2**) ($CDCl_3$)

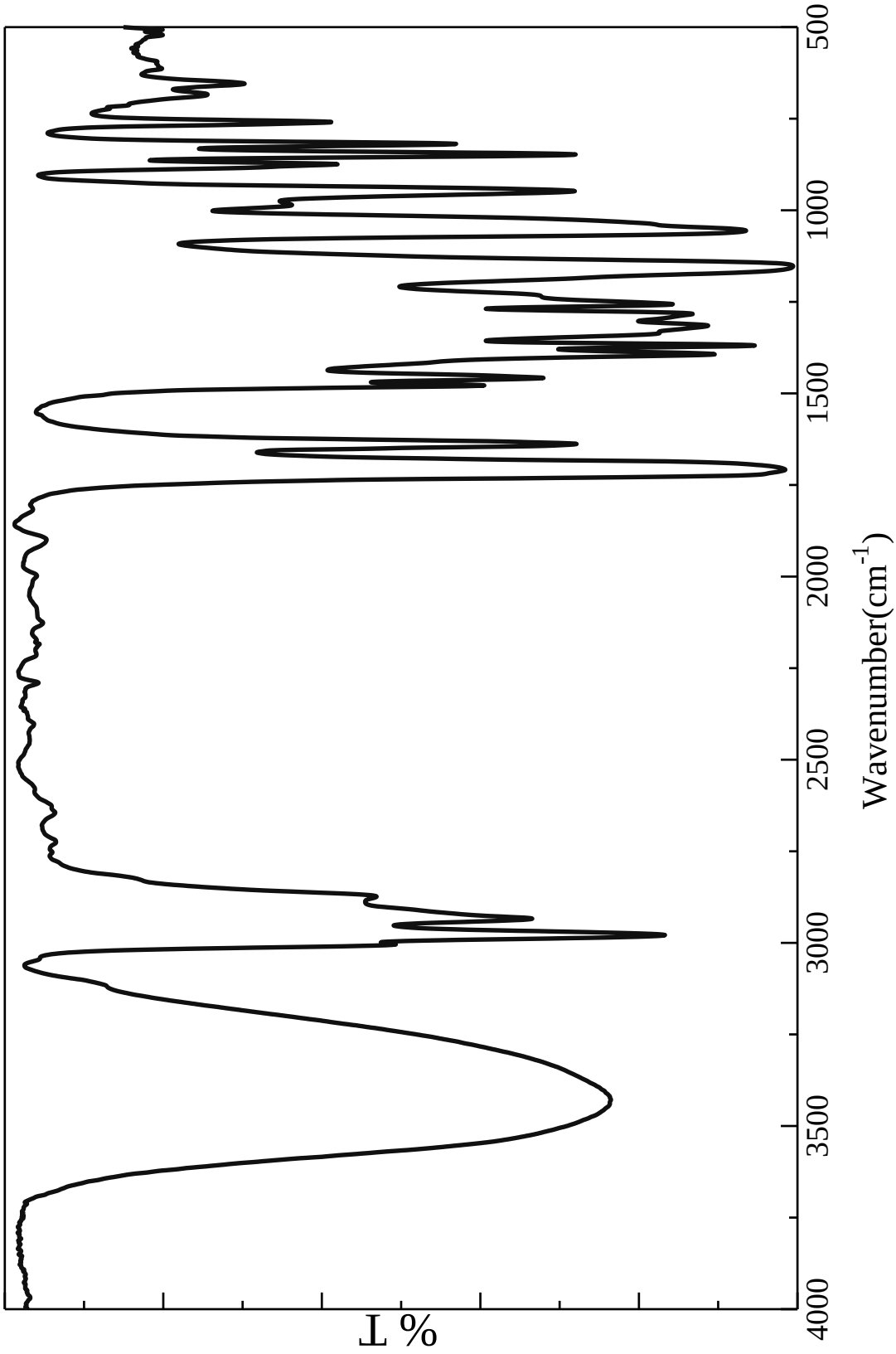


Fig. 3 IR spectrum of *tert*-Butyl 2-(Hydroxymethyl)acrylate (**2**) (NaCl)

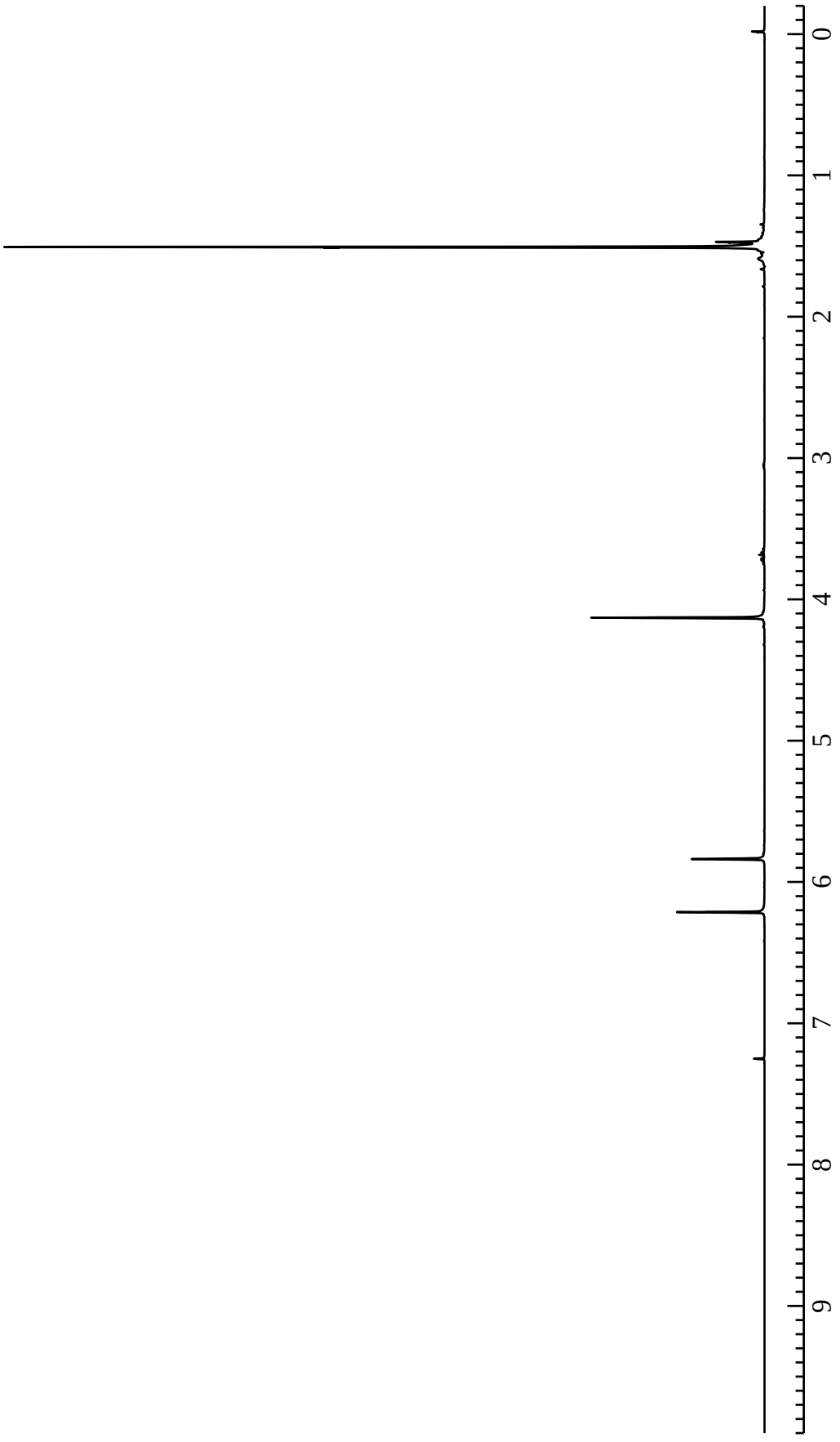


Fig. 4 ^{1}H NMR spectrum of *tert*-Butyl 2-(Bromomethyl)acrylate (**3**) ($CDCl_3$)

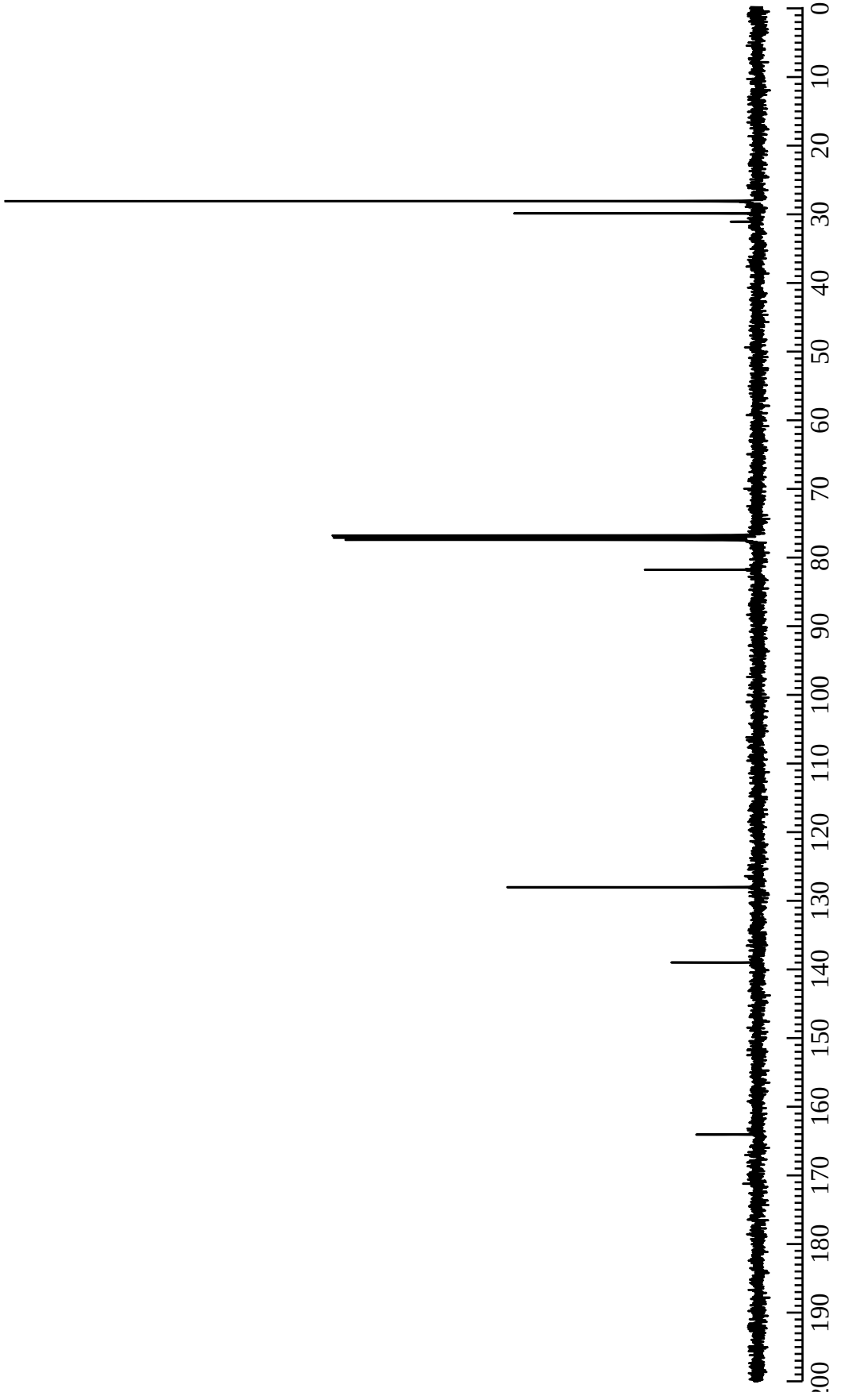


Fig. 5 ^{13}C NMR spectrum of *tert*-Butyl 2-(Bromomethyl)acrylate (**3**) ($CDCl_3$)

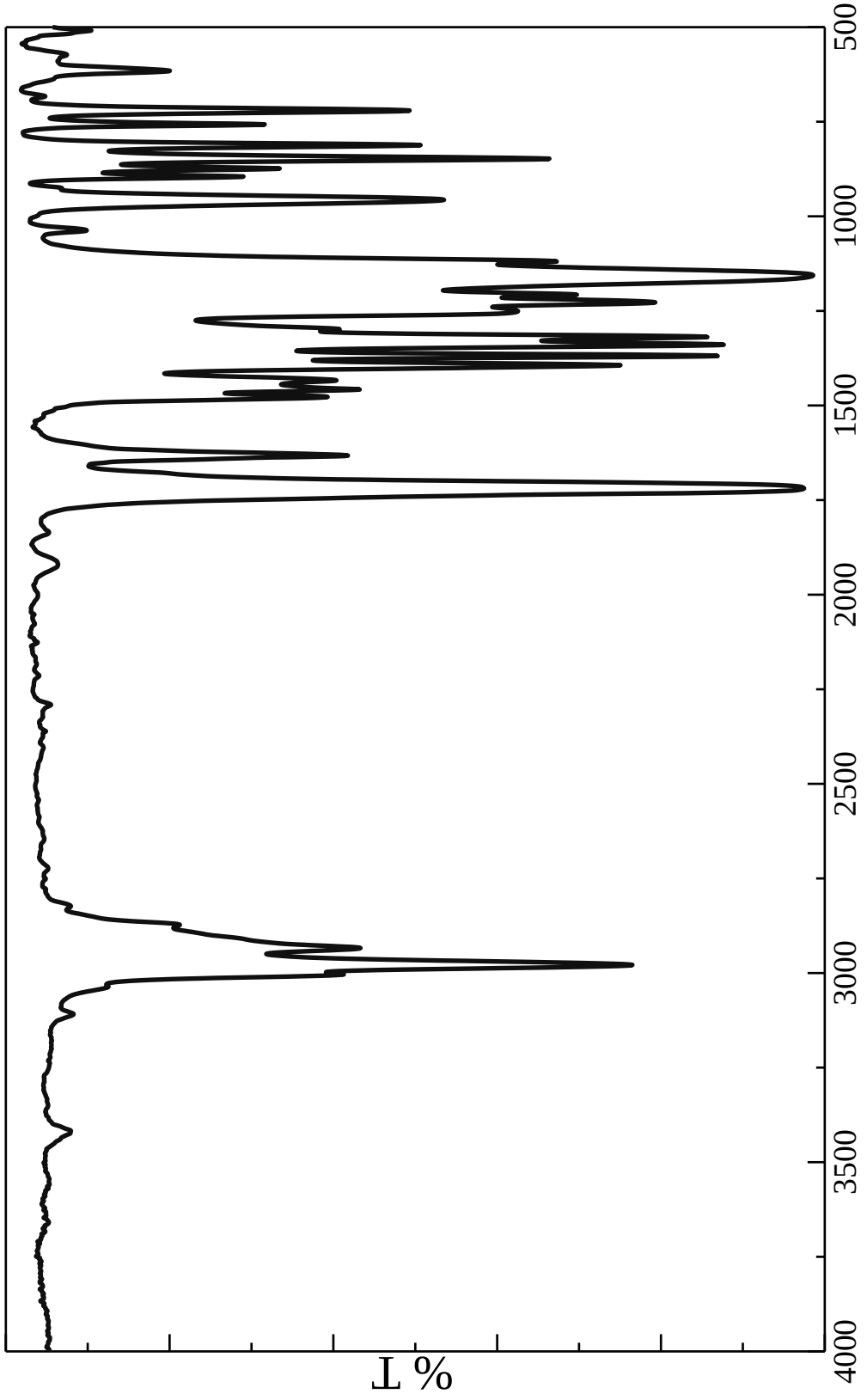


Fig. 6 IR spectrum of *tert*-Butyl 2-(Bromomethyl)acrylate (**3**) (NaCl)

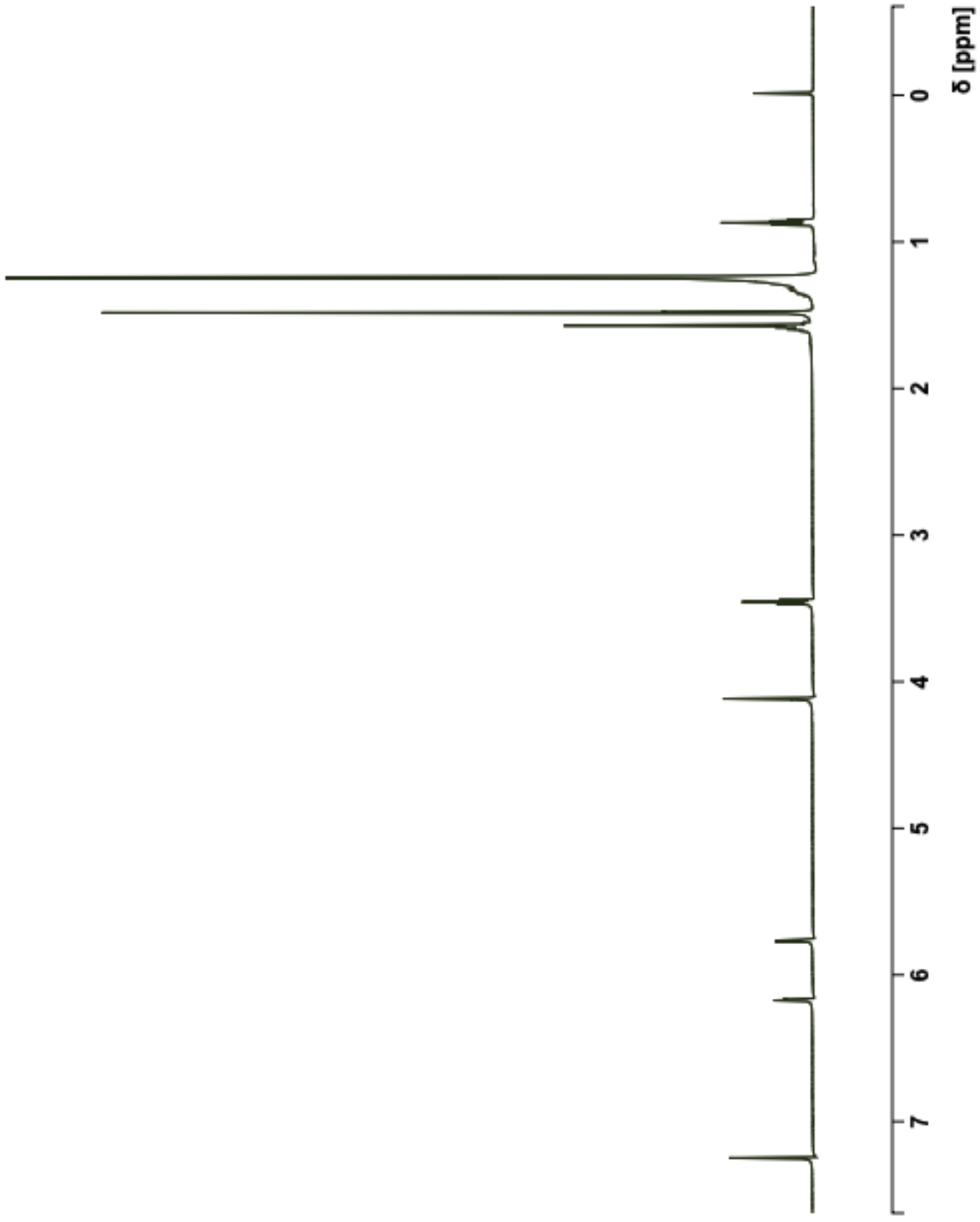


Fig. 7 ^{1}H NMR spectrum of *tert*-Butyl 2-(Octadecyloxymethyl)acrylate (**4**) ($CDCl_3$)

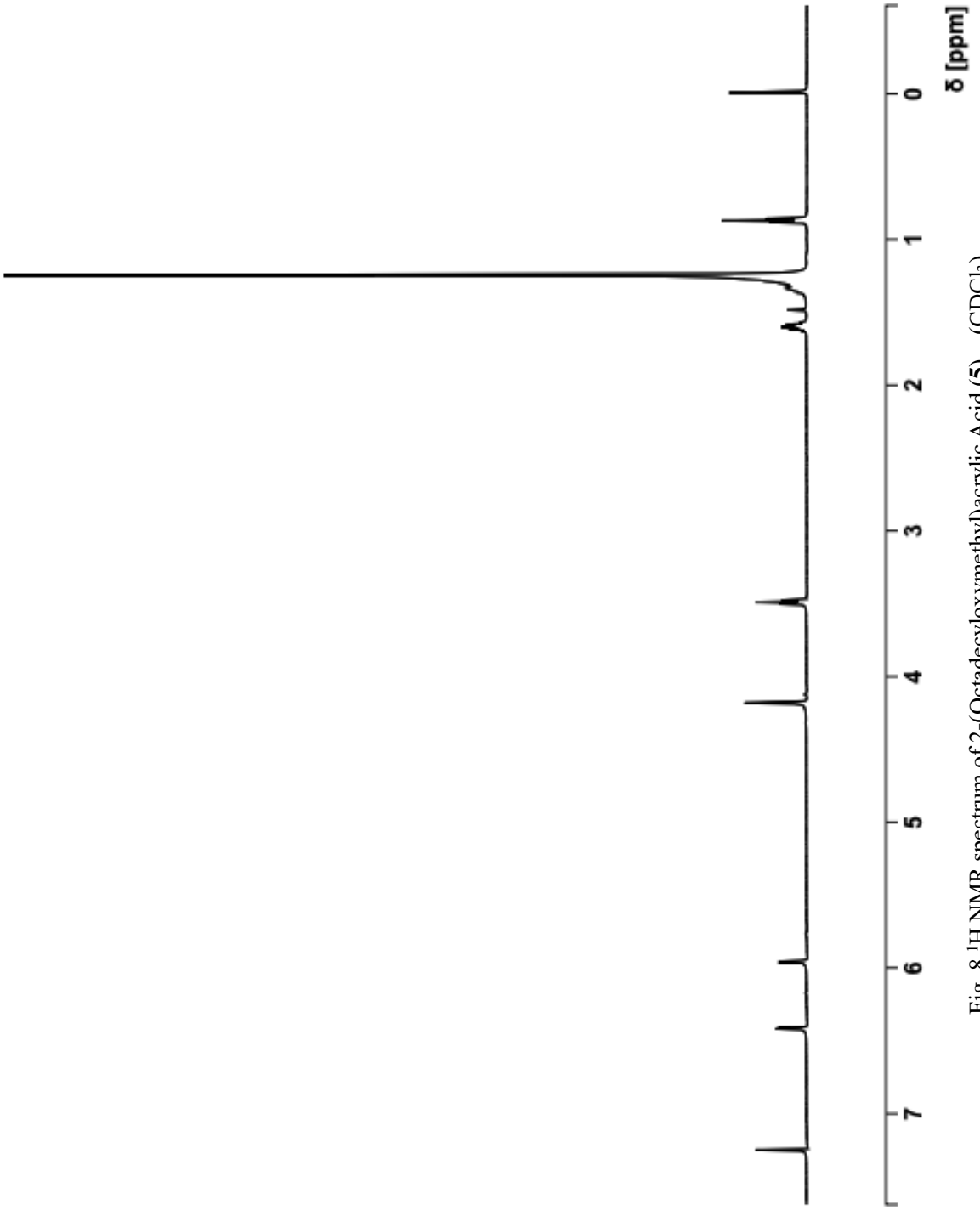


Fig. 8 ^{1}H NMR spectrum of 2-(Octadecyloxymethyl)acrylic Acid (**5**) ($CDCl_3$)

Fig. 9 ^{13}C NMR spectrum of 2-(Octadecyloxymethyl)acrylic Acid (**5**) ($CDCl_3$)

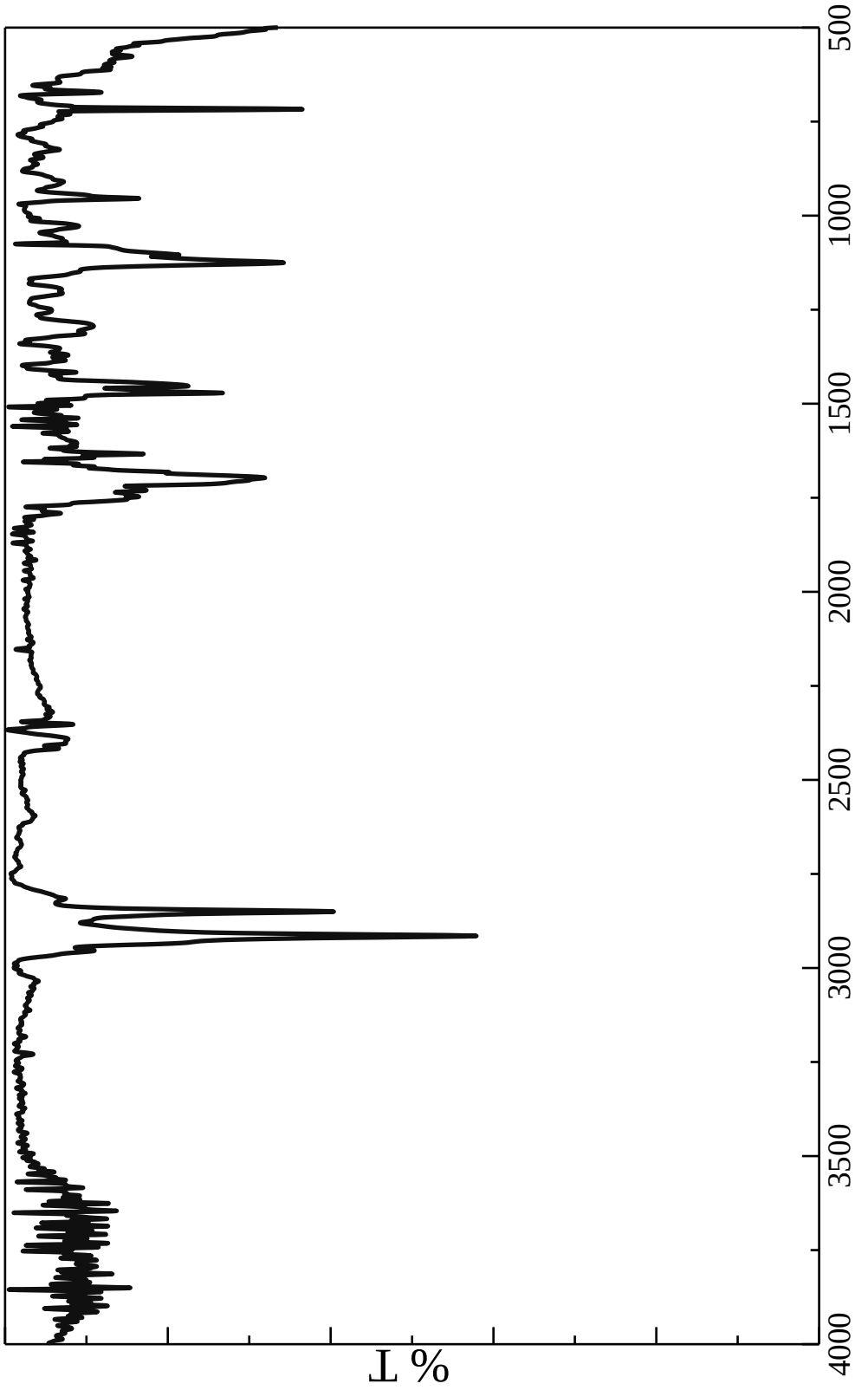


Fig. 10 IR spectrum of 2-(Octadecyloxymethyl)acrylic Acid) (**5**) ($CDCl_3$)

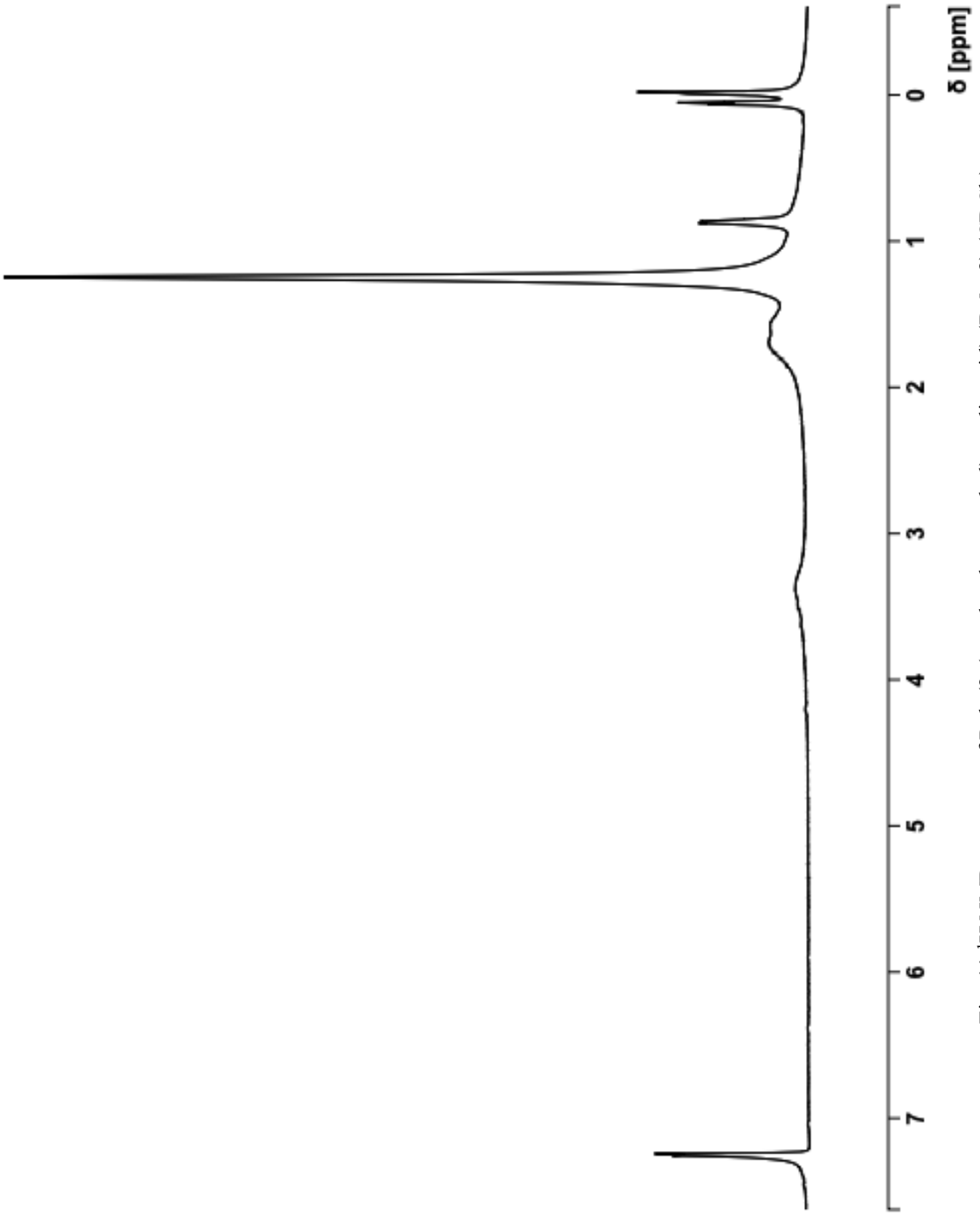


Fig. 11 ^{1}H NMR spectrum of Poly(2-(octadecyloxymethyl)acrylic acid) (**Poly-3**) ($CDCl_3$)

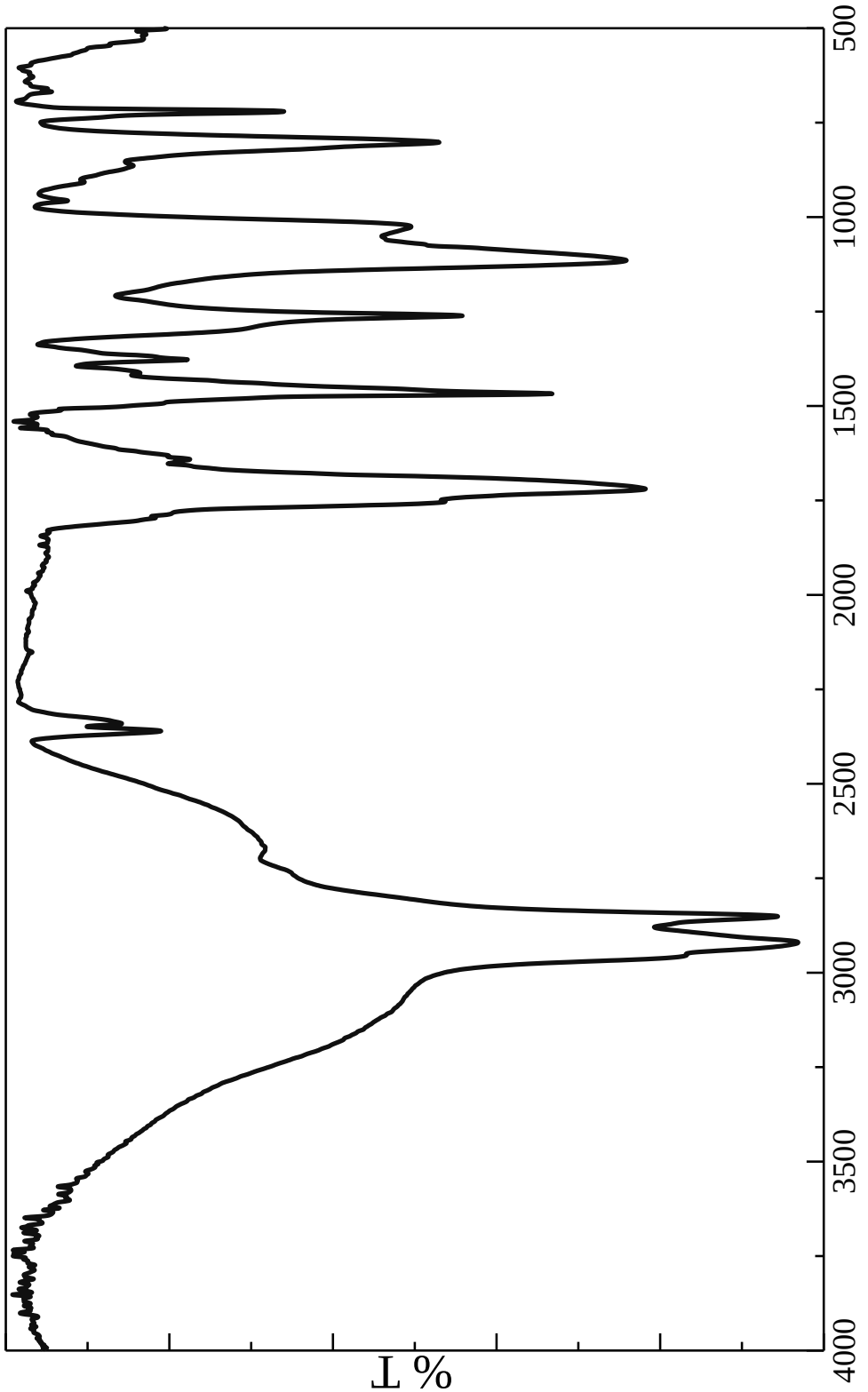
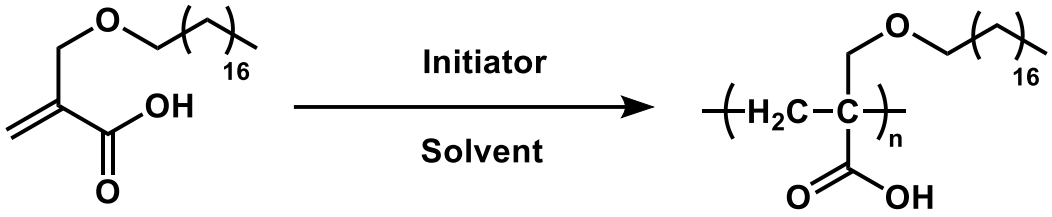


Fig. 12 IR spectrum of Poly(2-(octadecyloxymethyl)acrylic acid) (**Poly 3**) ($CDCl_3$)

CHAPTER 3 Results and Discussion

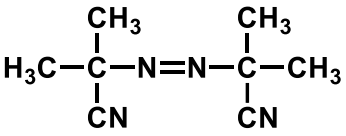
3.1 Radical Polymerization of 2-(Octadecyloxymethyl)acrylic Acid (5)



5 **Poly-3**

Table 1 Solution radical polymerization of 2-(Octadecyloxymethyl)acrylic Acid (**5**)

run	**5** mg (mmol)	Solvent ml	Initiator mg	[**5**] / [I]	Temp. °C	Time h	Yield mg (%)	Mn	Mw / Mn
1	200 (0.564)	$CHCl_3$ 0.74	AIBN 1.853	10	60	48	-	-	-
2	200 (0.564)	$CHCl_3$ 0.74	AIBN 1.853	10	60	48	0.13 (65.0)	11,300	2.75
3	200 (0.564)	$CHCl_3$ 1.5	AIBN 1.853	10	60	48	0.165 (82.65)	7,900	2.19



AIBN

The monomer and initiator were weighted into an ampoule tube, degassed by the freeze-thaw method, and radical polymerization was carried out. The ampoule tube was then allowed to react for 48 hours at 60 °C. The solution was then re-precipitated.

Run 1: After the reaction stopped, the monomer was re-precipitated with methanol and hexane. Unfortunately, the sample couldn't be purified. The polymer sample contained a lot of $CHCl_3$-insoluble parts, and the $CHCl_3$-soluble parts did not precipitate in hexane.

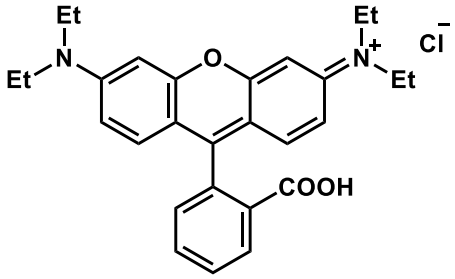
Run 2: The monomer was re-precipitated with hexane. The molecular weight of the sample shown in the GPC measurement is quite large.

Run 3: The polymerization process was performed with increased solvent. After 48 hours, the sample was reprecipitated with methanol and hexane. The hexane-soluble polymer was collected, evaporated, and examined.

3.2 Evaluation of Amphiphilicity of Poly(2-(octadecyloxymethyl)acrylic acid) (Poly-3)

3.2.1 Calibration curve for Rhodamine B

To confirm that **Poly-3** (Mn = 7,900) which obtained by radical polymerization formed reverse micelles, extraction experiments were performed using the water-soluble dye Rhodamine B. The calibration curve used in this study was adapted from the work of Junya Suzuki in their thesis, 'Effect of Substituent Structure on the Amphiphilic Properties of Poly(α-substituted acrylic acid)', completed at Mie University in 2021. This curve was chosen due to its relevance and applicability to the current research conditions.[6]



Rhodamine B λ_{max} = 553 nm

The linear equation was calculated to be y = 98.906x, and the decision function the R^2 value is 0.9963, which is close to 1 and thus considered reliable. In the following experiment, the concentration of Rhodamine B was calculated from the absorbance (A_{533}) detected by the UV-vis measurement using the calibration curve equation.

Table 2 Absorbance of Rhodamine B[6]

Rhodamine B Concentration (mM)	Absorbance (553 nm)
0.02	2.221
0.01	1.135
0.008	0.892
0.005	0.533
0.004	0.440
0.002	0.225
0.001	0.113
0.0008	0.085
0.0005	0.050
0.0004	0.039
0.0002	0.019

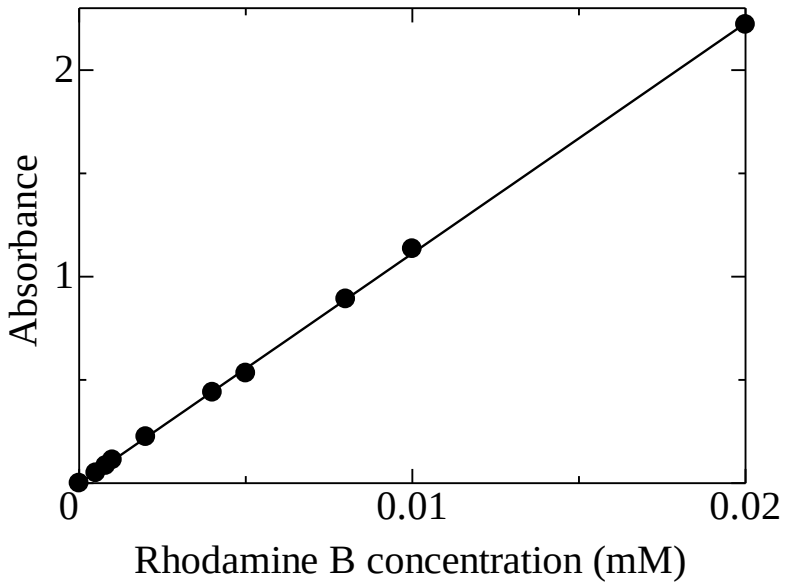


Figure 13 The calibration curve of Rhodamine B[6]

3.2.2 Extraction experiment of Rhodamine B

A 0.01 mM aqueous solution of Rhodamine B was prepared, and a hexane-only solution without polymer was used as 0 mM, while the hexane solutions of **Poly-3** were prepared at four different concentrations; 0.50 mM, 1.0 mM, 2.0 mM, and 5.0 mM.

4 mL each of 0.01 mM aqueous Rhodamine B solution and polymer solution were placed in a sample tube, and two solutions were mixed for 60 seconds using a vortex mixer, and the samples were allowed to stand for a while. The hexane layer was then transferred to a quartz cell for UV-vis measurement. Using the calibration curve, the concentration of Rhodamine B was calculated from absorbance $A_{533,}$ and the extraction rate was also calculated.

Table 3 Poly **5** Extraction rate of Rhodamine B

Sample	Polymer Concentration (mM)	Absorbance (553 nm)	Rhodamine B Concentration (mM)	Extraction ratio (%)
① RB 0.01 mM + Poly 0 mM	0	0	0	0
② RB 0.01 mM + Poly 0.50 mM	0.50	0.031	0.000031	3.1
③ RB 0.01 mM + Poly 1.0 mM	1.0	0.017	0.00017	1.7
④ RB 0.01 mM + Poly 2.0 mM	2.0	0.094	0.00095	9.5
⑤ RB 0.01 mM + Poly 5.0 mM	5.0	0.216	0.0022	21.8

The photos after the extraction of Rhodamine B are shown below. The upper layer is the hexane layer and the lower layer is the water layer.

0 mM 0.50 mM 1.0 mM 2.0 mM 5.0 mM

Figure 14 The extraction of Rhodamine B of **Poly-3** (Mn = 7,900)

As the concentration of the **Poly-3** increased, the upper layer became pinker and showed an increase in absorbance and extraction rate values, indicating that the extraction rate of Rhodamine B depended on the polymer concentration.

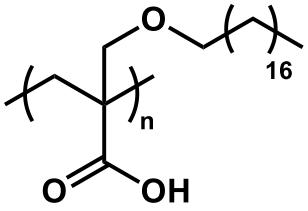
This suggests that **Poly-3** in hexane solution forms reverse micelles and encapsulates aqueous Rhodamine B solution.

3.3 Effect of Molecular Structure on Extractability

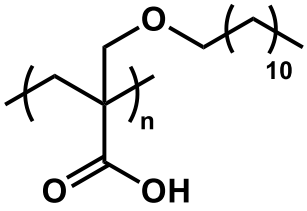
3.3.1 Poly(2-(Dodecyloxymethyl)acrylic acid) (**Poly-2**) and Poly(2-(Octadecyloxymethyl)acrylic acid) (**Poly-3**)

The extraction experiment of Rhodamine B was performed using **Poly-3** obtained by radical polymerization and its extraction rates were obtained. The comparison was done with **Poly-2** which was investigated in the previous study.[6]

The extraction rates of Rhodamine B were compared from polymers with different length chain structures to investigate how the hydrophobic portion introduced affects the extraction rate of the polymers.



Poly-3



Poly-2

Table 4 Extraction rates of Rhodamine B

Polymer Concentration (mM)	Absorbance (553 nm)		Extraction ratio (%)	
	Poly-3	**Poly-2**[6]	**Poly-3**	**Poly-2**[6]
0	0	0	0	0
0.50	0.031	0.058	3.1	5.9
1.0	0.017	0.082	1.7	8.3

2.0	0.094	0.150	9.5	15
5.0	0.216	0.255	21.8	26

Based on the result shown in Table 4, it does confirm that **Poly-3** can extract Rhodamine B the same as **Poly-2**. However, the extraction rates of **Poly-3** are lower compared to **Poly-2**. This may suggest that the longer chains are not necessarily able to attract more dye better than shorter chains.

Based on the values in Table 4, a graph was created with polymer concentration on the horizontal axis and extraction rate on the vertical axis.

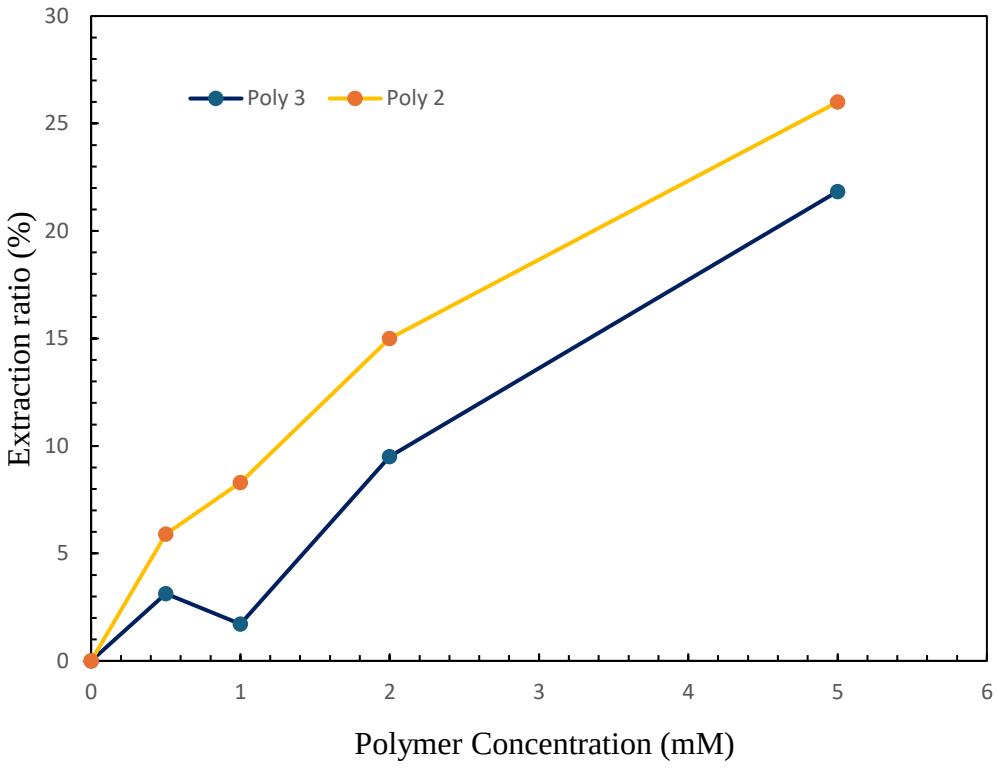


Figure 15 The extraction ratio of Rhodamine B

As the concentration of the polymer increased, the extraction rate also increased. However, for **Poly-3**, the extraction rate is not as great as **Poly-2**. This is probably due to the octadecyl-

substituted polymer may aggregate more in the hexane phase due to stronger hydrophobic interactions among the longer chains. This aggregation can reduce the effective surface area and accessibility for Rhodamine B to interact with the polymer.

Besides, the bulkier octadecyl groups might create steric hindrance, preventing efficient interaction and encapsulation of Rhodamine B. On the other hand, dodecyl groups, being shorter, may offer less steric hindrance, allowing better interaction with Rhodamine B.

Other than that, variations in experimental conditions, such as concentration, temperature, and mixing efficiency, could also affect the extraction process. It is possible that under the conditions of the experiment of **Poly-3**, the dodecyl group performed better.

CHAPTER 4 Conclusion

Amphiphilic homopolymer (**Poly-3**) was successfully synthesized by radical polymerization of α-substituted acrylic acid with octadecyl group (**5**) obtained by hydrolysis of α-substituted acrylic ester (**4**). The evaluation of amphiphilicity of **Poly-3** showed that **Poly-3** can extract Rhodamine B dye into the hexane layer. However, based on the comparison with **Poly-2**, **Poly-3** shows a lower extraction rate than that of **Poly-2**.

There are various possible reasons for this phenomenon, and one of the reasons may be that the octadecyl-substituted polymer may aggregate more in the hexane phase due to stronger hydrophobic interactions among the longer chains. The bulkier octadecyl groups also might create steric hindrance, preventing efficient interaction and encapsulation of the rhodamine B into the hexane layer.

References

1. Kimura, Y. and Terashima, T. Morphology transition of amphiphilic homopolymer self-assemblies in water triggered by pendant design and chain length. *Eur. Polym. J.* **139**, 110001 (2020).

2. Grégorio C. Recent developments in polysaccharide-based materials used as adsorbents in wastewater treatment. *Prog. Polym. Sci.* **30**, 38–70 (2005).

3. Kataoka, K., Harada, A. and Nagasaki, Y. Block copolymer micelles for drug delivery: design, characterization and biological significance. *Adv Drug Deliv. Rev.* **47**, 113–131 (2001).

4. Kuperkar, K., Patel, D., Atanase, L. I. and Bahadur, P. Amphiphilic Block Copolymers: Their Structures, and Self-Assembly to Polymeric Micelles and Polymersomes as Drug Delivery Vehicles. *Polymers* **14**, 4702 (2022).

5. Fried J. R. *Polymer Science and Technology Third Edition.* Prentice Hall (2013).

6. Suzuki, J. *Mie University master's thesis* (2021).

Acknowledgments

I would like to express my deepest gratitude to Professor Masataka Kubo for their invaluable guidance and support throughout my research. I am profoundly thankful to my supervisor, Associate Professor Takahiro Uno, whose constant encouragement and insightful feedback have been instrumental in shaping this thesis. I also extend my sincere appreciation to Assistant Professor Hazlina and Masashi Tamura for their unwavering assistance and dedication, ensuring that my experiments ran smoothly. This work would not have been possible without their collective efforts and expertise.

To my lab mates, Kazuki Kawai, Hashimoto Ranna, Tomoya Enoki, Tsuchihashi Tsubaki, and the rest of my laboratory members, I extend my heartfelt thanks for the camaraderie, stimulating discussions, and the collaborative environment we shared. Your support, both academically and personally, has enriched my research experience in countless ways.

I would also like to express my heartfelt gratitude to my parents, Sazali bin Abas@Zahari, Salmiah binti Abd Rahman, and Allahyarham Roslan bin Karimudin whose unconditional love, unwavering support, and sacrifices have been the bedrock of my academic pursuits. Their belief in me has been a constant source of motivation and strength. To my siblings, thank you for your encouragement, understanding, and financial aid. Your patience and support have been invaluable throughout this challenging journey.

I am deeply thankful to my friends, Amira, Farah, Kiho, Hazirah, and all my Malaysian friends, for their continuous support, understanding, and encouragement. Your presence in my life has made this journey more enjoyable and fulfilling.

Lastly, shout out to Seventeen for keeping me sane during my master's journey.

This thesis is a testament to the collective efforts, encouragement, and support of all these remarkable individuals. Thank you all for making this achievement possible.