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# APPENDICES

# APPENDIX A

## A. Degree of Polymerization of Poly(diethylbenzalmalonate vinyl ether)

The weight average molecular weight ($\overline{M}w$) of poly(diethylbenzalmalonate vinyl ether) obtained by gel permeation chromatrography technique (GPC) was 1943.

The average degree of polymerization was calculated by the following equation:

$$\text{Average degree of polymerization} = \frac{\overline{M}w \text{ of polymer}}{\text{MW of monomeric unit}}$$

Since MW of monomeric units was 290.13,

$$\text{Therefore, the average degree of polymerization of this compound} = \frac{1943}{290.13}$$

$$= 6.7$$

Structure of synthesized poly(diethylbenzalmalonate vinyl ether) can therefore, be expressed as follows:

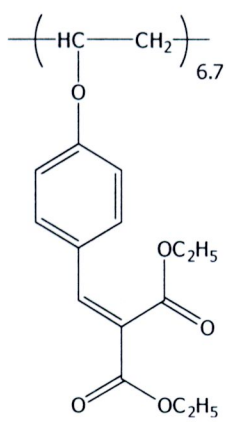


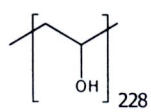


Figure A.1 Structure of poly(diethylbenzalmalonate vinyl ether).

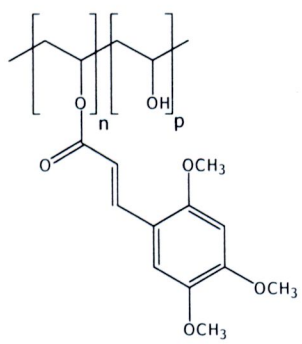
**B. Substitution Degree of Cinnamoyl Groups in Poly[(Vinyl 2,4,5-Trimethoxy cinnamate)(Vinyl Alcohol)] Copolymer**

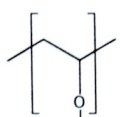
**B.1 Calculation from Weight Average Molecular Weight ($\overline{M}w$) Data**

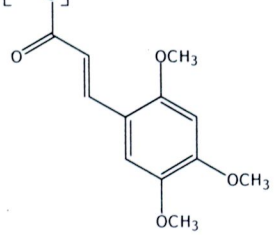
The GPC analysis of poly[(vinyl 2,4,5-trimethoxycinnamate)(vinyl alcohol)] copolymer (90°C grafted compound) gave weight average molecular weight ($\overline{M}w$) of 31557. From the molecular weight of the grafted product and the weight average molecular weight of the starting material (PVA; $\overline{M}w$ = 10024), the average degree of cinnamoyl substitution of this compound could be calculated.

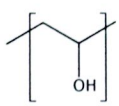
- One mole of PVA ($\overline{M}w$ = 10024) consists of 228 hydroxyl units 


Given general structure of poly[(vinyl 2,4,5-trimethoxycinnamate)(vinyl alcohol)] as follows:




Where, MW of  monomeric unit is 264 and




MW of  monomeric unit is 44,

We can obtain $(264 \times n) + (44 \times p) = 31557$ ----------(1)

$n + p = 228; \quad p = 228-n$ ----------(2)

(1) and (2) $[(264 \times n) + 44x (228-n)] = 31557$

$220\ n = 21569$

$\therefore\ n \sim 98, p = 228-98 = 130$

From the above calculation, poly[(vinyl 2,4,5-trimethoxycinnamate)(vinyl alcohol)] copolymer (90°C grafted product) can be depicted as follows:

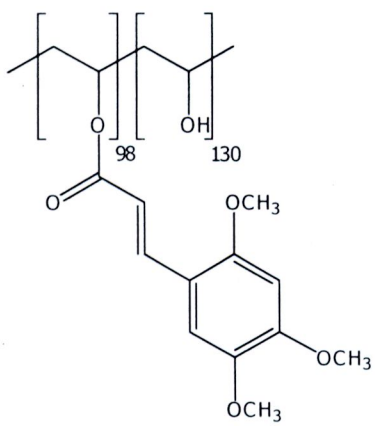



Figure A.2 Structure of poly[(vinyl 2,4,5-trimethoxycinnamate)(vinyl alcohol)] copolymer.

**B.2 Calculation from UV Absorption Data**

Since molar absorptivity (ε) of 2,4,5-trimethoxycinnamoyl moiety are 12,400 $M^{-1}cm^{-1}$ ($\lambda_{max}$ = 290 nm) and 14,200 $M^{-1}cm^{-1}$ ($\lambda_{max}$ = 349 nm)[31] and molar absorptivity (ε) of the grafted product are 1,180,000 $M^{-1}cm^{-1}$ ($\lambda_{max}$ = 284 nm) and 1,220,000 $M^{-1}cm^{-1}$ ($\lambda_{max}$ 342 nm), calculation of degree of substitution can be done as follows:

$$\text{Average degree of cinnamoyl substitution} = \frac{\varepsilon\text{'s of a grafted polymer}}{\varepsilon\text{'s of 2,4,5-trimethoxycinnamoyl moiety}}$$

$$\text{Therefore, calculated at UVB region} = \frac{1{,}180{,}000}{12{,}400} \sim 96 \text{ unit}$$

$$\text{And when calculated at UVA region} = \frac{1{,}220{,}000}{14{,}200} \sim 86 \text{ unit}$$

From the above calculation, poly[(vinyl 2,4,5-trimethoxycinnamate)(vinyl alcohol)] copolymer (90°C grafted product) can be expressed as follows:

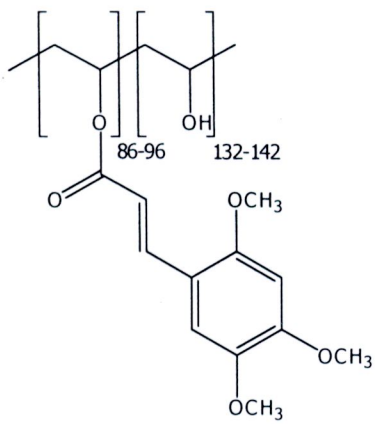



Figure A.3 Structure of poly[(vinyl 2,4,5-trimethoxycinnamate)(vinyl alcohol)] copolymer.

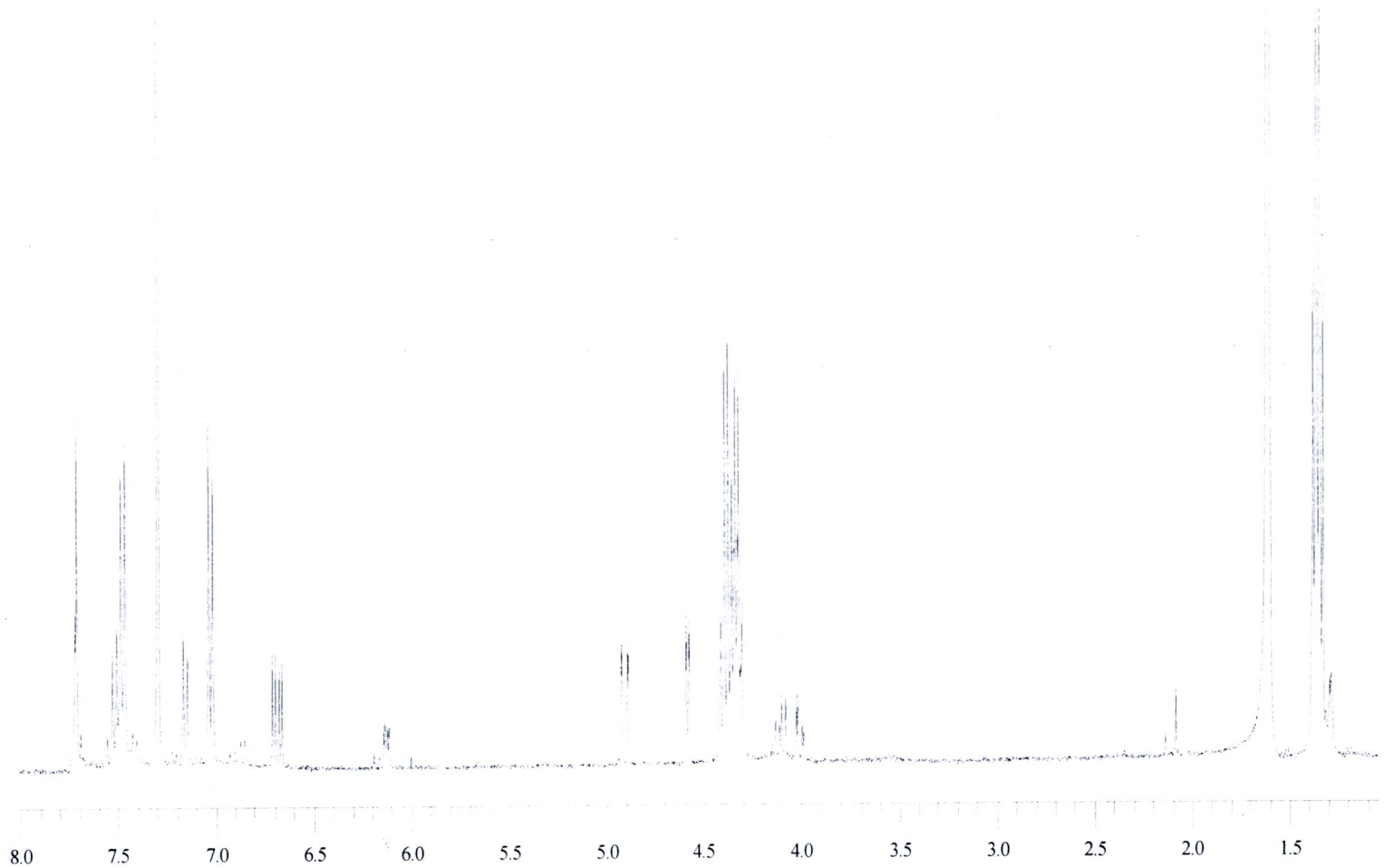



Figure B.1 $^{1}$H-NMR spectrum of poly(diethylbenzalmalonate vinyl ether).

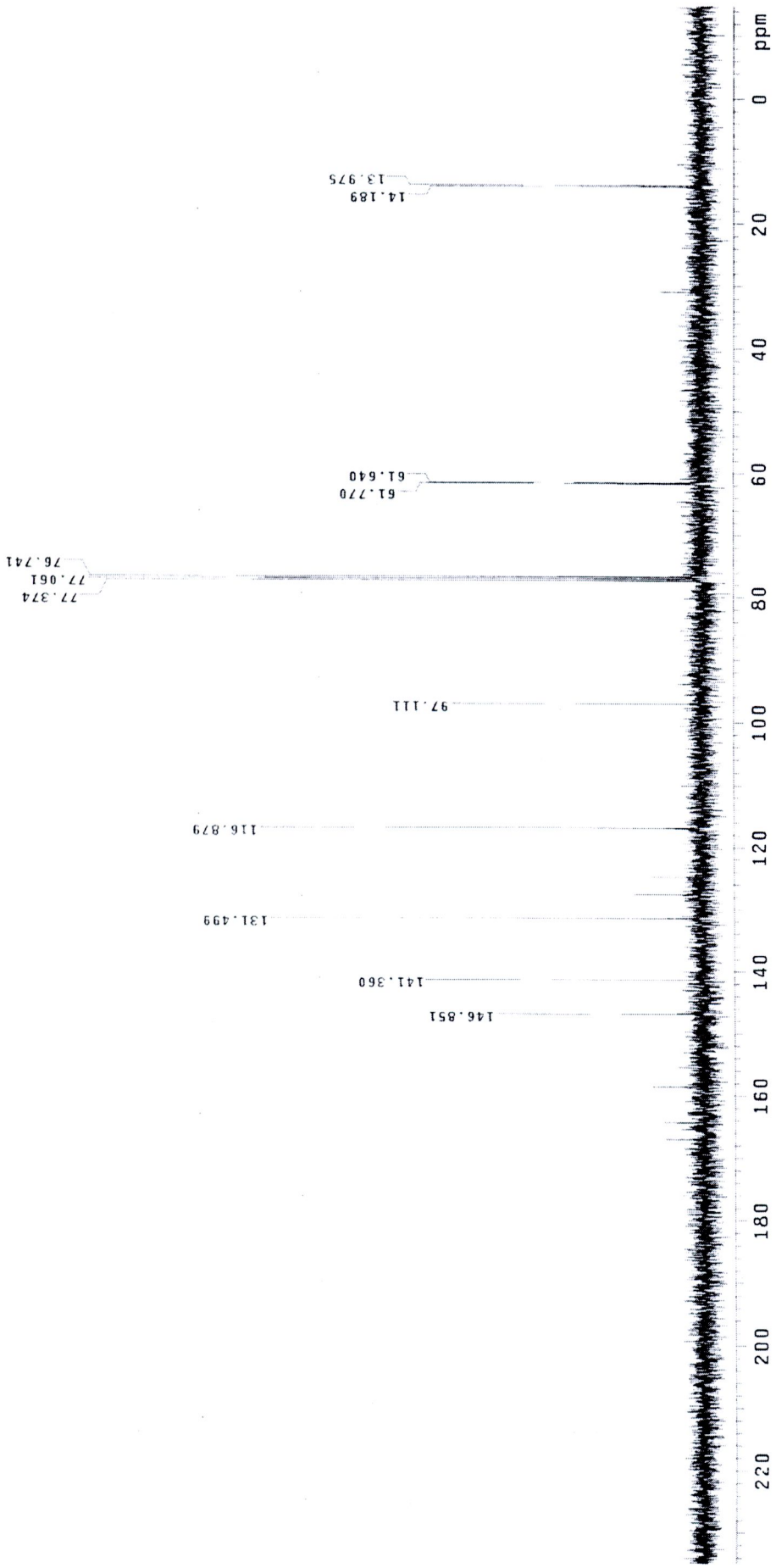



Figure B.2 $^{13}$C-NMR spectrum of poly(diethylbenzalmalonate vinyl ether).

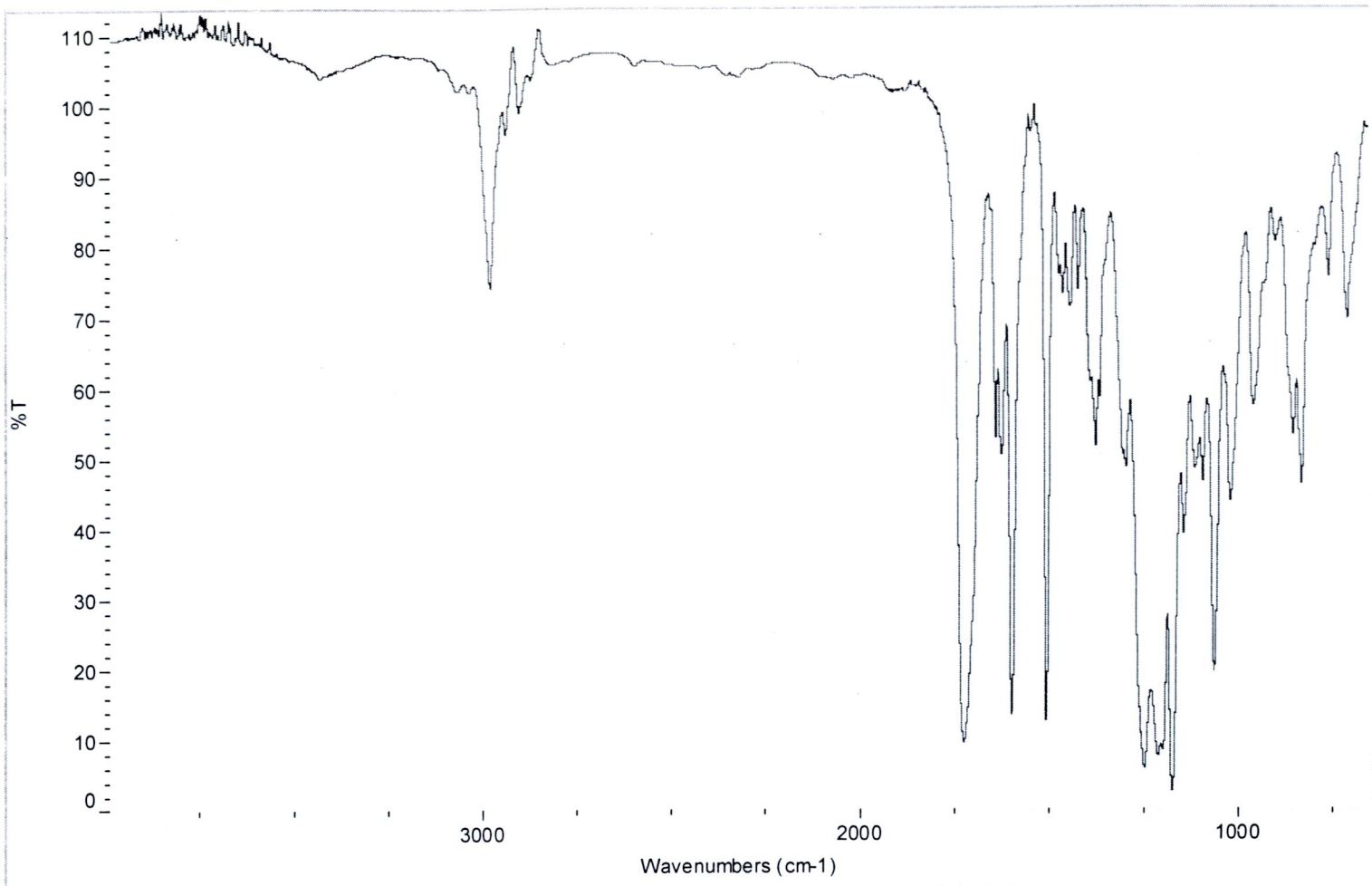
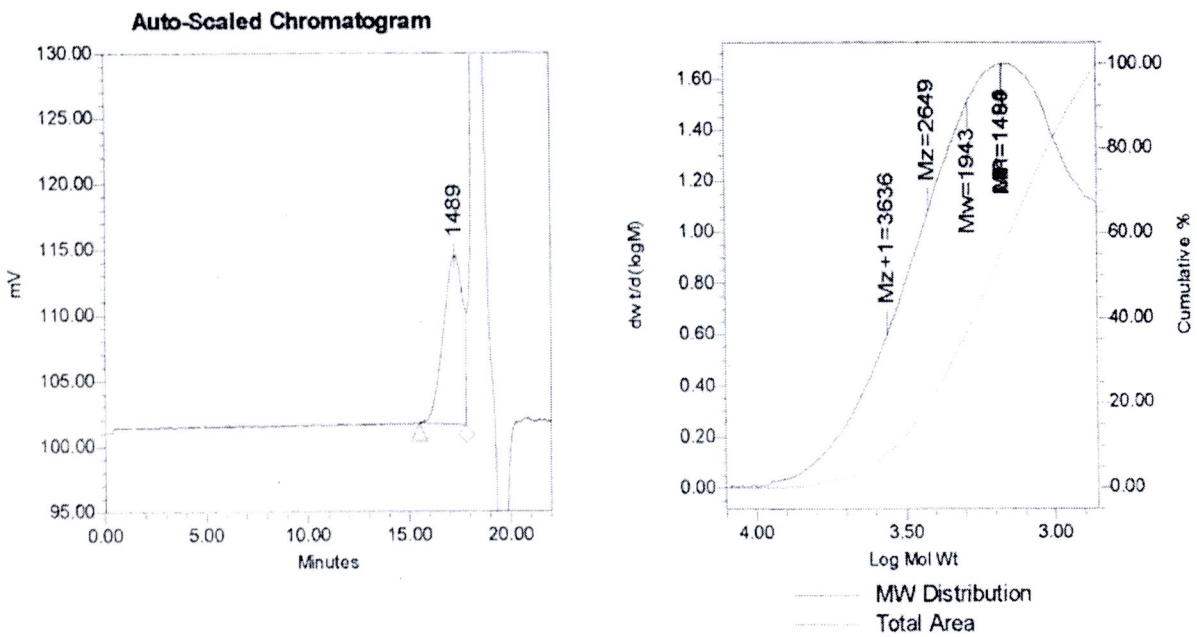



Figure B.3 IR spectrum of poly(diethylbenzalmalonate vinyl ether).

## Sample Information

| | |
|---|---|
| Sample Name | poly(diethylbenzalmalonate vinyl ether) |
| Vial | 1 |
| Injection Volume | 100.00 µl |
| Channel | SATIN |
| Run Time | 22.00 Minutes |




**Peak Results**

| | Mn | Mw | MP | Mz | Mz+1 | Polydispersity |
|---|---|---|---|---|---|---|
| 1 | 1494 | 1943 | 1489 | 2649 | 3636 | 1.300438 |

Figure B.4 GPC chromatogram of poly(diethylbenzalmalonate vinyl ether).

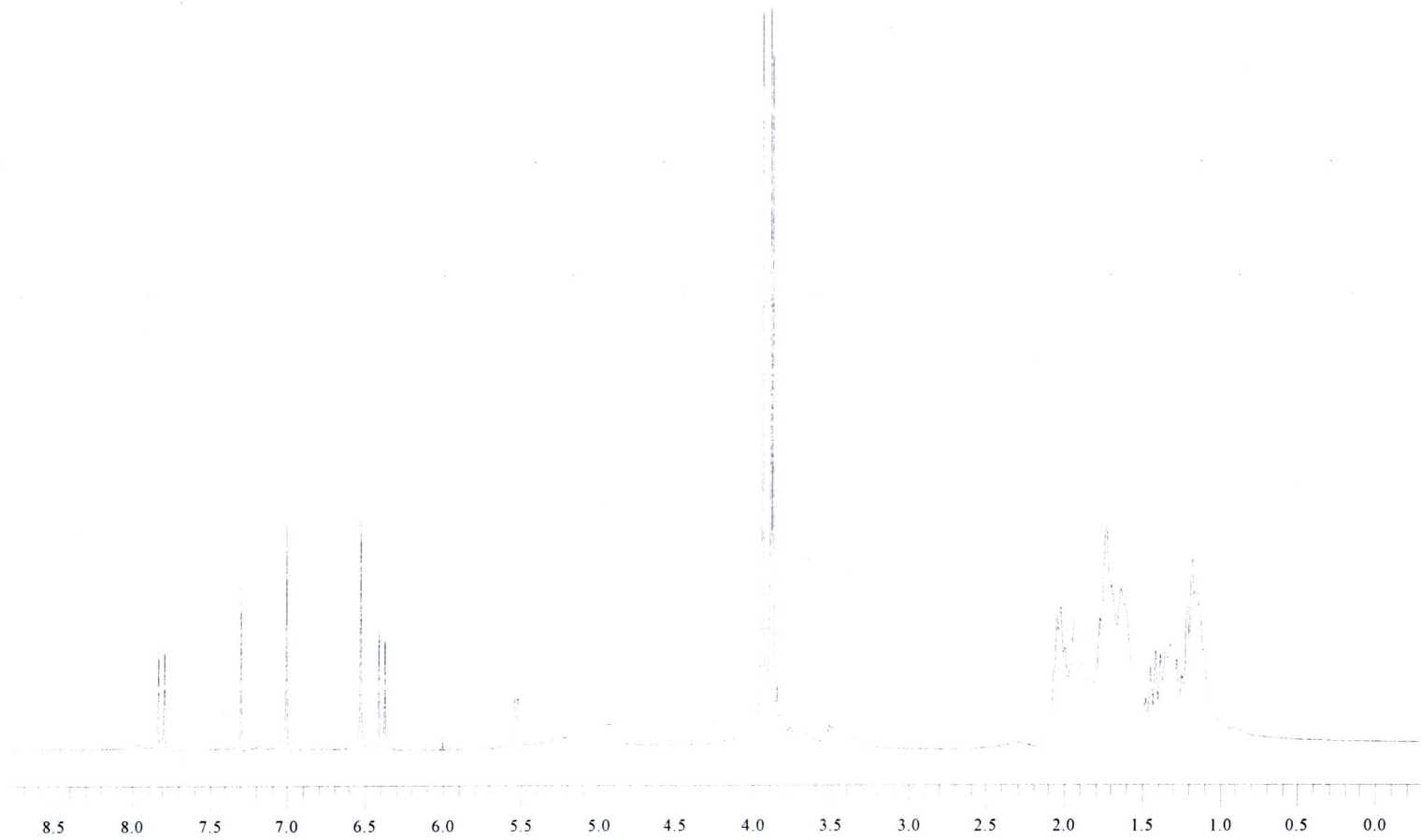



Figure B.5 $^{1}$H-NMR spectrum of poly[(vinyl 2,4,5-trimethoxycinnamte)(vinyl alcohol)] copolymer.

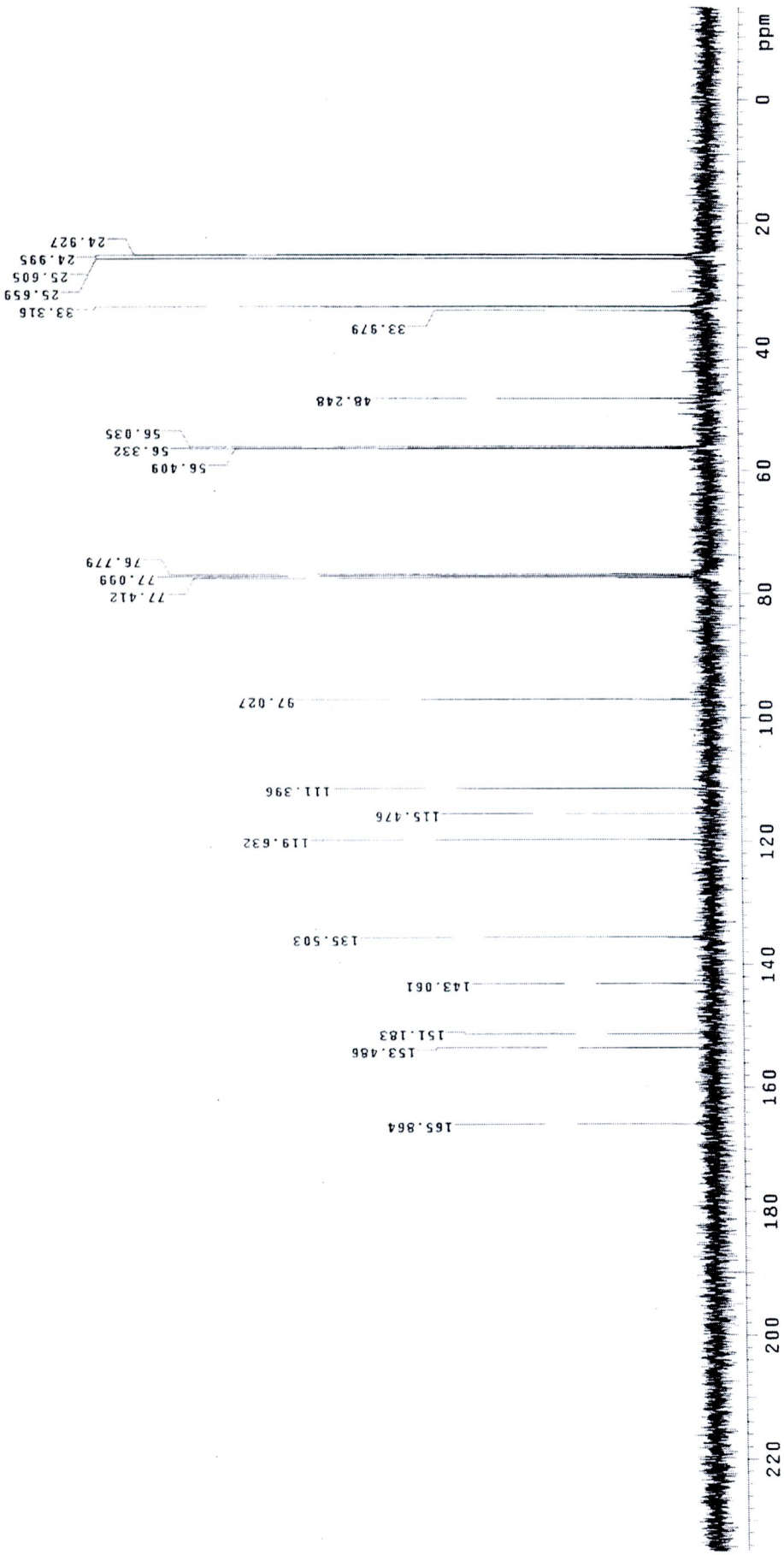



Figure B.6 $^{13}$C-NMR spectrum of poly[(vinyl 2,4,5-trimethoxycinnamte)(vinyl alcohol)] copolymer.

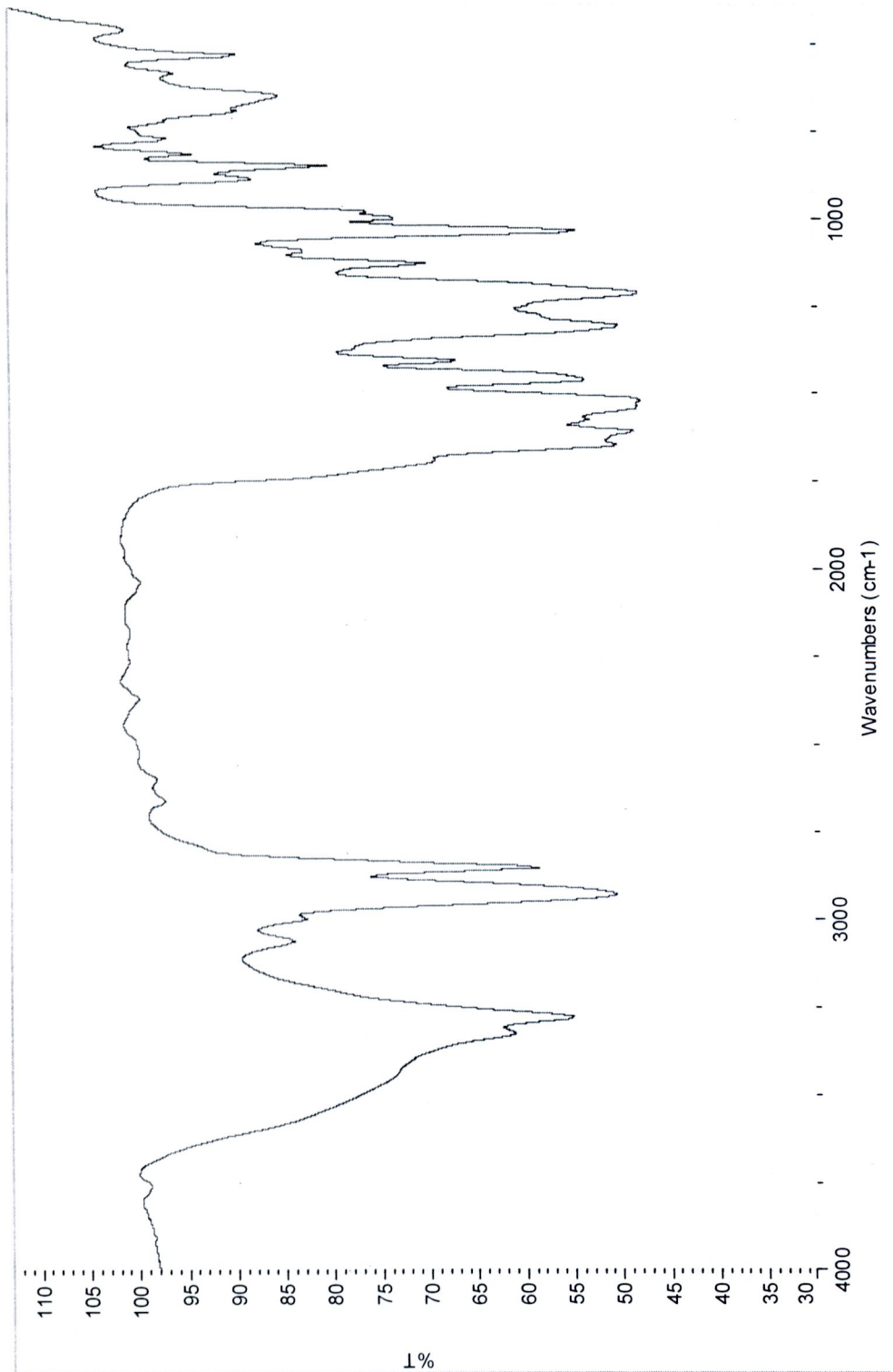
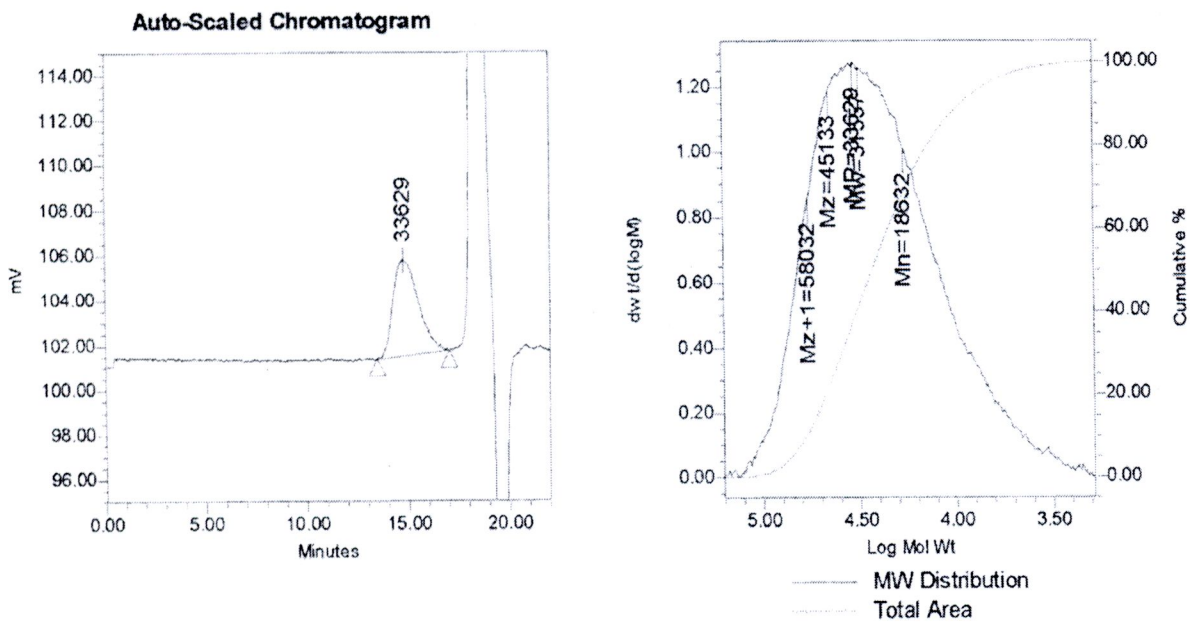



Figure B.7 IR spectrum of poly[(vinyl 2,4,5-trimethoxycinnamte)(vinyl alcohol)] copolymer.

## Sample Information

| | |
|---|---|
| Sample Name | poly[(vinyl 2,4,5-trimethoxycinnamate)(vinyl alcohol)] copolymer |
| Vial | 2 |
| Injection Volume | 100.00 µl |
| Channel | SATIN |
| Run Time | 22.00 Minutes |




**Peak Results**

| | Mn | Mw | MP | Mz | Mz+1 | Polydispersity |
|---|---|---|---|---|---|---|
| 1 | 18632 | 31557 | 33629 | 45133 | 58032 | 1.693749 |

Figure B.8 GPC chromatogram of poly[(vinyl 2,4,5-trimethoxycinnamate)(vinyl alcohol)] copolymer.

# VITA

Miss Piyawan Hirunsupachot was born on April 17, 1981 in Bangkok. She got a Bachelor Degree of Science in Chemistry from Chulalongkorn University in 2002. After that, Miss Hirunsupachot has been a graduate student pursuing a Master Degree in Organic Chemistry at Chulalongkorn University. During her study towards the Master's Degree, Miss Hirunsupachot was awarded a teaching assistant scholarship by the Faculty of Science during 2003-2005. She was also awarded a research grant from the Graduate School, Chulalongkorn University.

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