



Chapter II

Experimental

2.1. General Information

2.1.1. Instruments

- Infrared Spectrophotometer : Perkin Elmer, model 1430
- Fourier-Transformed NMR spectrometer : Jeol, model JNX-FX 90Q
- Atomic Absorption Spectrophotometer : Shimadzu, model AA-670
- Gas Chromatography : Shimadzu, model 9A
- Inductively Coupled Plasma Emission Spectrometer : Shimadzu, model ICPS 50
- Elemental Analyzer : Perkin Elmer, Model Perkin Elmer 240 CHNO analyzer
- Differential Thermal Analyzer : Shimadzu Thermal Analysis Instrument DT-30
- Melting point : John-Fisher electrothermal melting point apparatus with cover glass sample holder and are uncorrected.

2.1.2. Reagents

1. Organotin compounds ; dimethyltin dichloride, dibutyltin dichloride and diphenyltin dichloride, reagent grade, E. Merck, Germany : used without further purification.
2. Alkyl dihalide ; 1,4 dibromobutane and 1,6 dibromobenzene, reagent grade, Fluka, Switzerland, used without further purification.
3. Anhydrous tetrahydrofuran ; removed trace of water by refluxing with sodium metal and distilled before use.
4. Anhydrous benzene ; treated in the same manner as tetrahydrofuran.
5. Magnesium turning ; reagent grade, Fluka, Switzerland.
6. Solvent : hexane, methanol, ethyl acetate ; commercial grade, were distilled before used.
7. *o*-Dichlorobenzene ; reagent grade ; E. Merck, Germany, used without further purification.
8. Pyridine ; reagent grade, BDH, England, used without further purification.
9. Petroleum ether ; reagent grade, BDH, England, used without further purification
10. *p*-Toluenesulfonic acid (Toluene-4 sulfonic acid monohydrate); reagent grade, Fluka, Switzerland, used without further purification.

11. Iodine crystal
12. Sodium metal
13. Ammonium chloride
14. Adipic acid ; reagent grade, Fluka, Switzerland,
used without further purification
15. Malonic acid ; reagent grade, Fluka, Switzerland,
used without further purification
16. N,N Dimethyl formamide (DMF); reagent grade,
Fluka, Switzerland, used without further purification



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2.2. Synthesis of organotin monomers

2.2.1. Synthesis of organotin monomers by using iodine as initiator.

2.2.1.1. 1,4 butylene-bis(dibutyltin chloride)

Placed magnesium turning (2.05 g, 84.3 mmol) in a 500 ml. flask fitted with a condenser, stirrer, dropping funnel and inlet and outlet tubes for dry nitrogen. After the reaction was initiated by adding a small amount of iodine, the 1,4 dibromobutane (9.12 g, 42.2 mmol) in 250 ml. tetrahydrofuran was added dropwise. When the addition was completed, refluxing was continued for an additional 1 hour. Tetrahydrofuran was distilled off from the reaction mixture using Dean-Stark apparatus. Benzene (200ml.) was added and then dibutyltin dichloride (25.6 g, 84.3 mmol) was added dropwise with vigorous stirring. The reaction mixture was refluxed at 80°C for 3 hours. The excess Grignard reagent was decomposed by addition of a small amount of saturated ammonium chloride solution. Chloroform (10 ml.) was added in order to dissolve product in organic layer. The organic layer was separated and dried with sodium sulfate anhydrous for 2 hours. The organic layer was evaporated at reduced pressure and residue was dissolved in tetrahydrofuran (75 ml.). The solution in tetrahydrofuran was extracted with a saturated aqueous solution of ammonium chloride, evaporated to dryness and the residue crystallized from petroleum ether affording 13.52 g (30%) as a white solid with m.p. 112-114°C.

IR (KBr pellet) max cm^{-1} : 2950, 2925, 2875, 2850
 (aliphatic C-H bond) ; 1200
 (C-Sn bond), 1420
 (C-H bending, CH_2),
 1370 (C-C, bending)

^1H -NMR(90 MHz, CDCl_3 , ppm) : 0.94(12H, t, $J=6.4$, CH_3) ;
 1.20-2.00(32H, m)

^{13}C NMR(CDCl_3) ppm : 13.6 ($-\text{CH}_3$), 25.8, 26.7,
 26.9, 27.6, 27.8 (CH_2)

Elemental analysis Calcd for $\text{C}_{20}\text{H}_{44}\text{Sn}_2\text{Cl}_2$ (592.92) :

C 40.51% ; H 7.50% ; Sn 40.04% ;
 Cl 11.96%

Found C 40.56% ; H 7.46% ; Sn 40.01% ;
 Cl 11.97%

2.2.1.2. 1,4-phenylene-bis(dibutyltin chloride)

1. To the preform Grignard reagent, prepared from (5g, 21.19 mmol) of p-dibromobenzene and (1.18g, 48.54 mmol) magnesium turning in 250 ml. of dry tetrahydrofuran, was added dropwise with vigorous stirring a solution of dibutyltin dichloride (15.6g, 51.34 mmol) in tetrahydrofuran 75 ml. The

mixture was refluxed for 3 hours, evaporated to dryness in vacuo and the residue extracted with hot benzene. The combined extracted was evaporated to dryness and the residue was dissolved in tetrahydrofuran. The solution in tetrahydrofuran was extracted with a saturated aqueous solution of ammonium chloride, and the organic portion was evaporated to dryness to obtain a residue which was recrystallized from petroleum ether to give the title compound in 10.8% yield, m.p. 108-110°C.

2. *p*-Bis(chlorobis-butylstannyl) benzene was prepared in the same manner as 1,4-butylene-bis(dibutyltin chloride) by using *p*-dibromobenzene (5g, 21.19 mmol) and magnesium (1.25g, 51.42 mmole) in 250 ml. tetrahydrofuran and dibutyltin dichloride (15.6g, 51.34 mmole) the title compound was obtained in 13.4% yield, m.p. 108-110°C.

Elemental Analysis calcd. for

Found C 35.76% : H 6.70% : Sn 44.85%

IR(KBr) max cm^{-1} : 2980-2850 (C-H, str, alkane),
1450-1420(=CH₂ bending), 1200 (C-Sn)

¹H NMR(90 MHz, CDCl₃, ppm) : 0.94(12H, t, J=6.4 Hz) ;
1.20-1.64(12H, m) ; 1.67-2.09(12H, m)

¹³C NMR (22.5 MHz, CDCl₃, ppm) : 13.6, 26.5, 26.6, 27.1,
27.3, 32.3, 32.9

2.2.1.3. 1,4-butylene-bis(dimethyltin chloride)

The procedure was the same as in the synthesis of 1,4-butylene-bis(dibuthyltin chloride). By using magnesium turning (2.26g, 92.92 mmole), 1,4-dibromobutane (9.12g, 42.24 mmole) and dimethyltin dichloride (20.41g, 92.92 mmole), the title compound was obtained as a colourless liquid (b.p. 85-87°C/4 mmHg.) in 10.9% yield

IR(KBr cell) max cm^{-1} : 2950, 2925, 2875, 2850
(aliphatic C-H), 1200 (C-Sn)

^1H NMR(CDCl_3) ppm : 0.92 (12H, d, CH_3), 1.3 (8H, m)

^{13}C NMR(22.5 MHz, CDCl_3 ppm) : 13.5(CH_3) ; 17.4, 27.7, 28.0

Elemental analysis calcd : for $\text{C}_8 \text{H}_{20} \text{Sn}_2 \text{Cl}_2$ (424.56) :
C 22.63% : H 4.76% : Sn 55.91% :
Cl 16.70%

2.2.1.4. Product obtained from the reaction of 1,4 dibromobutane with diphenyltin dichloride.

The procedure was the same as in the synthesizing of 1,4 butylene-bis dimethyltin chloride. By

using magnesium turning (2.26g, 92.92 mmole), 1,4 dibromobutane (9.12 g, 42.24 mmole) and dipheyltin dichloride (21.39 g, 81.84 mmol), the title compound was obtained in 15.1% yield as a white solid, m.p. 192-193°C.

IR (KBr pellet) max cm^{-1} : 2000-1667 (overtone of Aromatics) ;
3100-3000 (C-H Stretch : aromatic) ;
1200 (C-Sn)

^1H NMR (90 MHz, CDCl_3 , ppm) : 7.33-7.87 (m)

^{13}C NMR (22.5 MHz, CDCl_3 , ppm) : 128.7, 128.8, 137.2, 137.4

Elemental Analysis calcd :

Found : C 66.44%, H 4.58%, Sn27.90%

2.2.2. Synthesis of organotin monomers by using di-Grignard reagent of 1,2-dibromoethane.

2.2.2.1. Synthesis of Di-Grignard reagent [15, 17]

To a suspension of magnesium turning (1.18g, 48.54 mmole) in dry tetrahydrofuran (15 ml.), was added 1,2-dibromoethane 0.5 ml, and the mixture stirred at 15-20°C until evolution of ethylene gas was evident. Stirring was then continued for 5 min. The tetrahydrofuran was removed and

replaced by fresh tetrahydrofuran 30 ml. and the mixture stirred rapidly at 15-20°C. To this was added dropwise a solution of 1,4-dibromobenzene (5g, 21.19 mmole) in dry tetrahydrofuran (250 ml.) over a period of 3.5 hours. The solution become pale green and after addition was completed, stirring was continued and dried with sodium sulfate anhydrous for 2 hours. The organic layer was analyzed by gas chromatography in order to determine the amount of benzene. The gas chromatography indicated that the di-grignard reagent was obtained.

Gas chromatographic (conditions : capillary column, length 25 m. coated with OV 101 ; column temperature 50°C, injection temperature 175°C, nitrogen carrier gas flow rate 1 ml/min. and using FID detector).

2.2.2.2. Synthesis of 1,4-phenylene-bisdibutyltin chloride)

1,4-Phenylene-bisdibutyltin chloride) was prepared via a di Grignard reaction by method of 2.2.2.1. Tetrahydrofuran from Grignard synthesis was distilled off from the reaction mixture using Dean-Stark apparatus, (benzene 200 ml.) was added and dimetyltin dichloride (10.24g, 46.63 mmol) was added dropwise with vigorous stirring. The reaction mixture was refluxed at 80°C for 3 hours. The excess Grignard reagent was decomposed by the additional of a small amount of saturated ammonium chloride solution. Chloroform (10 ml.) was added in

order to dissolved the reaction products. The organic layer was separated and dried with sodium sulfate anhydrous for 2 hours. The organic layer was evaporated at diminish pressure and residue was dissolved in tetrahydrofuran (75 ml.). The solution in tetrahydrofuran was washed with saturated aqueous solution of ammonium chloride. The solvent was then evaporated and the residue was crystallized from petroleum ether to yield 1.54 g (15.03%) yield a white solid with m.p. 160-162°C.

IR(KBr) max cm^{-1} : 1200 (C-Sn) ; 2000-1667
(overtone of Aromatics) ;
2962, 2962 (-CH₃).

¹H NMR(90 MHz, CDCl₃, ppm) : 1.18 (6H, s, CH₃) ; 1.25
(6H, s, CH₃) ; 7.3 (4H, m)

¹³C NMR(CDCl₃) ppm : 13.8 (-CH₃) ; 17.2, 125.8, 127.6, 128.5, 131.5

Elemental Analysis calculated for C₁₀H₁₆Cl₂Sn₂ (444.53) :

C 27.02% ; H 3.63% ; Cl 15.95% ;
Sn 53.40%

Found : C 26.3% ; H 3.6% ; Cl 16.10% ;
Sn 54.00%

2.3. Preparation of Condensation polymerization.

2.3.1. Synthesis of Condensation polymerization between 1,4-Butylene bis-(dibutyltin chloride) and adipic acid.

1,4-Butylene bis-(dibutyltin chloride) (1.38 g, 0.23 mmol) and adipic acid (0.34 g, 0.23 mmol) were dissolved in benzene (15 ml.), tetrahydrofuran (15 ml.), *o*-dichlorobenzene (15 ml.). The solutions were flushed with oxygen-free nitrogen and heated in a heating mantle maintain at 80°C, 67°C, 180°C for 20 hrs. The solution were poured into ethyl acetate to precipitate the polyester.

Solvent	Solution in ethyl acetate
THF	viscous
Benzene	viscous
<i>o</i> -dichlorobenzene	white Solid

2.3.1.1. Model without catalyst.

1,4-butylene bis-(dibutyltin chloride) and adipic acid were dissolved in *o*-dichlorobenzene (15 ml.). The solution was purged with nitrogen for 30 min. The solution was

Table 2. Showed mole ratios of reactant and %yield of polymer in the model system without Catalyst.

time (hrs)	Sample No.	1,4 BDD* (g)	Adipi acid (g)	Poly(1,4-BDDAA)** (g)	yield %
10	W10 1:1	1.3807	0.3387	0.5466	39.59
	W101: 1.5	1.4454	0.5357	0.5268	36.45
	W10 1:2	1.4465	0.7166	0.3293	22.70
15	W15 1:1	1.5122	0.3712	0.6419	42.45
	W15 1:1.5	1.5226	0.5726	0.5815	38.19
	W15 1:2	1.4921	0.7425	0.4838	32.42
20	W20 1:1	1.4465	0.7166	0.9907	68.49
	W20 1:1.5	1.1313	0.4215	0.4793	42.37
	W20 1:2	1.4604	0.7172	0.5271	36.09

* 1,4.BDD is 1,4-butylene-bis(dibutyltin chloride)

** Poly(1,4-BDDAA) is Poly(1,4-butylene-bis(dibutyltin adipate))

2.3.1.2. Polymerization in the presence of p-toluenesulfonic acid.

The reaction was carried out in the same manner to that of 2.3.1.1. except that p-toluenesulfonic acid (0.05g, mmol) was used as catalyst. The ratios of monomers and the yields of polymers were tabulated in Table 3.

Table 3. Showed the mole ratio of reactants and yield of polymers in the presence of p⁻ toluenesulfonic acid

time (hrs)	Sample No.	1,4 BDD* (g)	Adipi acid (g)	Poly(1,4BDDAA)** (g)	yield %
10	10C 1:1	1.4334	0.3547	0.4656	32.48
	10C 1:1.5	1.4902	0.5732	0.4498	30.19
	10C 1:2	1.3671	0.6738	0.31.69	23.18
15	15C 1:1	1.4338	0.3606	0.6760	47.15
	15C 1:1.5	1.5900	0.5984	0.5645	35.50
	15C 1:2	1.7612	0.8654	0.6372	36.18
20	20C 1:1	1.4668	0.3674	0.9210	62.79
	20C 1:1.5	1.4250	0.5345	0.9003	63.18
	20C :1.2	1.7877	0.8861	0.5830	32.61

* 1,4-BDD is 1,4-butylene-bis-(dibutyltin chloride)

Poly(1,4-BDDAA) is Poly(1,4-butylene-bis-(dibutyltin) adipate)

2.3.1.3. Polymerization in the presence of pyridine.

The reaction was carried out in the same manner to that of 2.3.11. except that pyridine (0.7 ml., mmol) was used. The mole ratio of monomers and yield of polymers were tabulated in Table 4.

Table 4. Showed the mole ratio of reactants and yields of polymers in the presence of pyridine.

time (hrs)	Sample No.	1,4 BDD* (g)	Adipic acid (g)	Poly(1,4-BDDAA)** (g)	yield %
10	P10 1:1	1.5549	0.3849	0.5668	36.45
	P10 1:1.5	1.5781	0.5920	0.5078	32.18
	P10 1:2	1.6181	0.4025	0.4905	30.31
15	P15 1:1	1.8892	0.4748	0.7963	42.15
	P15 1:1.5	1.7426	0.6476	0.6237	35.79
	P15 1:2	1.7795	0.8838	0.6291	35.35
20	P20 1:1	1.6756	0.4210	1.090	65.07
	P20 1:1.5	1.8525	0.6883	0.0407	56.15
	P20 1:2	1.7576	0.8770	0.8463	48.15

* 1,4-BDD is 1,4-butylene-bis-(dibutyltin chloride)

* Poly(1,4 BDDAA is Poly(1,4-butylene-bis-(dibutyltin adipate)

2.3.2. Polymerization of 1,4-butylene-bis-(dibutyltin chloride) with malonic acid.

These polymers were prepared from 1,4 butylene bis (dibutyltin chloride) and malonic acid in o-dichlorobenzene (15-ml.). The solution was flushed with nitrogen for 30 min before heating at 140°C for 20 hrs. The polymers were precipitated in ethyl acetate, filtered, dried and weighed.

IR (KBr) max cm^{-1} ; 2950, 2875, 2850 (aliphatic C-H) ; 1600 (C=O) ;
1500-1450 (CH_2 bending)

time (hrs)	Sample No.	1,4-BDD* (g)	Malonic a (g)	Poly(1,4-BDDMA)** (g)	Pyridine (ml)	yield %
20	M20 1:1	1.6962	0.3274	1.1100	-	65.54
20	M20 1:1P	1.7976	0.3749	1.1268	0.5	62.18

* 1,4-BDD is 1,4-butylene- bis-(dibutyltin chloride)

** Poly(1,4-BDDMA) is Poly(1,4-butylene-bis-(dibutyltin malonate)

2.3.3. Polymerization of 1,4-Butylene bis-(dibutyltin chloride) with malonic acid in DMF.

These polymers were prepared from 1,4-butylene bis-(dibutyltin chloride) with malonic acid in N, N-Dimethylformamide (DMF). The solution was flushed with nitrogen 30 min. before heating at 153°C for 20 hours. The polymer was precipitated in ethyl acetate, filtered, dried and weighed.

time (hrs)	Sample No.	1,4-BDD (g)	Malonic a (g)	Poly(1,4-BDDMA)** (g)	Pyridine (m)	yield %
20	P201:1	1.6842	0.2978	0.4126	-	24.50
20	P201:1P	1.5756	0.2712	0.4285	0.5	27.20

* 1,4 BDD is 1,4-Butylene-bis-(dibutyltin chloride)

** Poly(1,4 BDDAA) is Poly(1,4-Butylene-bis-(dibutyltin adipate)

2.4. Reaction between organotin monomers with sodium hydroxide.

2.4.1. Poly(1,4-butylene-bis-(dibutyltin) oxide)

Dissolved 1,4-butylene-bis-(dibutyltin chloride) (0.75 g, 1.26 mmol) in tetrahydrofuran (5 ml.) at 10-15°C and 0.1 N, NaOH (10 ml.) was added dropwise. After the addition was

2.3.3. Polymerization of 1,4-Butylene bis-(dibutyltin chloride) with malonic acid in DMF.

These polymers were prepared from 1,4-butylene bis-(dibutyltin chloride) with malonic acid in N, N-Dimethylformamide (DMF). The solution was flushed with nitrogen 30 min. before heating at 153°C for 20 hours. The polymer was precipitated in ethyl acetate, filtered, dried and weighed.

time (hrs)	Sample No.	1,4-BDD (g)	Malonic a (g)	Poly(1,4-BDDMA)** (g)	Pyridine (m)	yield %
20	P201:1	1.6842	0.2978	0.4126	-	24.50
20	P201:1P	1.5756	0.2712	0.4285	0.5	27.20

*1,4 BDD is 1,4-Butylene-bis-(dibutyltin chloride)

**Poly(1,4 BDDAA) is Poly(1,4-Butylene-bis-(dibutyltin adipate)

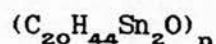
2.4. Reaction between organotin monomers with sodium hydroxide.

2.4.1. Poly(1,4-butylene-bis-(dibutyltin) oxide)

Dissolved 1,4-butylene-bis-(dibutyltin chloride) (0.75 g, 1.26 mmol) in tetrahydrofuran (5 ml.) at 10-15°C and 0.1 N, NaOH (10 ml.) was added dropwise. After the addition was

completed, stirring was continued for 20 min. This solution was filtered in order to separate white solid. The white solid was dried and weighed 0.68 g, 90.67% yield.

Elemental Analysis for

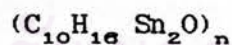


Calcd ;	C 44.62% ; H 8.26% ; Sn 44.14% ; O 2.98%
Found ;	C 44.89% ; H 8.12% ; Sn 44.37% ; O 2.62%

2.4.2. Poly(1,4-Phenylene-bis-(dimethyltin) oxide)

A similar reaction was carried out with 1,4-phenylene bis-(dimethyltin chloride) (0.6 g, 1.35 mmol). The white solid (0.5 g, 83.33% yield) was obtained.

Elemental analysis for



Calcd	C 30.81% ; H 4.15% ; Sn 60.94% ; O 4.10%
Found	C 30.75% ; H 4.28% ; Sn 60.75% ; O 4.19%

2.5. Analysis of polymer composition.

2.5.1. Determination of Tin in Polymers.

2.5.1.1. Principle

The polymer is decomposed by wet-ashing with mixed $\text{H}_2\text{SO}_4\text{-HNO}_3$, and tin is determined in its inorganic form either volumetrically, photometrically or by Atomic Absorption Spectroscopy (A.A.S.) and Inductively Coupled Plasma Emission Spectrometer (I.C.P.S.). For this study, the A.A.S. and I.C.P.S. technics were used.

2.5.1.2. Method.

The sample ca. 20 mg. was transferred to a suitable beaker and 10-20 ml. of H_2SO_4 (conc.) was added and then HNO_3 (conc.) was added dropwise 20 drops at the first stage and warmed, if necessary, to start the reaction. The addition of HNO_3 was continued so that an excess acid (denoted by copious brown fumes) was always present. Eventually the beaker was placed on the hot plate and wet-ashing was continued until all the organic matter was decomposed and a colourless or pale yellow solution was obtained. Then 20 ml. distilled water was added, boiled and evaporated to fuming again. The solution was then colourless, if it was not, additional 1 ml. HNO_3 and 0.5 ml. HClO_4 was added and heated to produce fuming again. The

digestion of polymers took about 24 hours to complete. For the determination of tin by A.A.S. and I.C.P.S, care must be taken that H_2SO_4 concentration was the same in all samples including the standards.

2.5.1.3. Preparation of standard solution and plotting the tin calibration curves.

Stannous chloride standard solution, 1000 ppm, for A.A.S. (75 ml.) was pipetted into a 250 ml. volumetric flask, and double distilled water was added to bring the volume up to 250 ml. The stock solution concentration became 300 ppm. The stock solution (50 ml.) was pipetted into four volumetric flasks and diluted with distilled water to a final concentrations of 50, 100, 150 and 200 ppm. The concentrations of standard solutions for calibration curves were 50, 100, 150, 200 and 300 ppm. The λ of tin is 286.3 nm.

2.6. Characterization of Monomers and Polymers.

2.6.1. Infrared (IR) Measurement

Infrared (IR) Spectra of Monomer and Polymers were recorded using Perkin-Elmer Infrared Spectrophotometer model 1430. This model can detect wavelength 4000-200 nm. The solid polymers and monomers were examined by using KBr pellet. The liquid samples were recorded as neat samples using KBr cell.

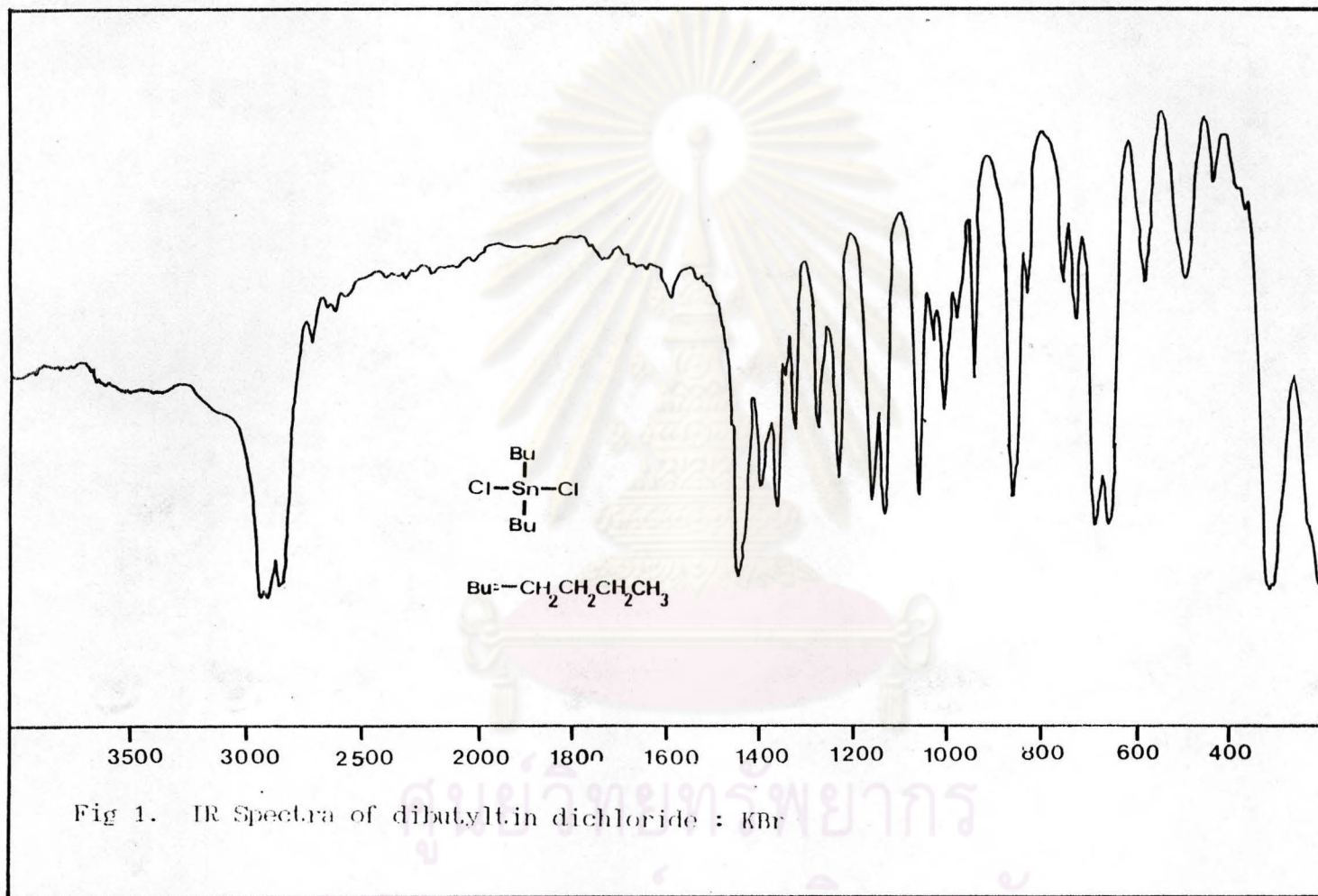
2.6.2. Nuclear Magnetic Resonance NMR Measurement

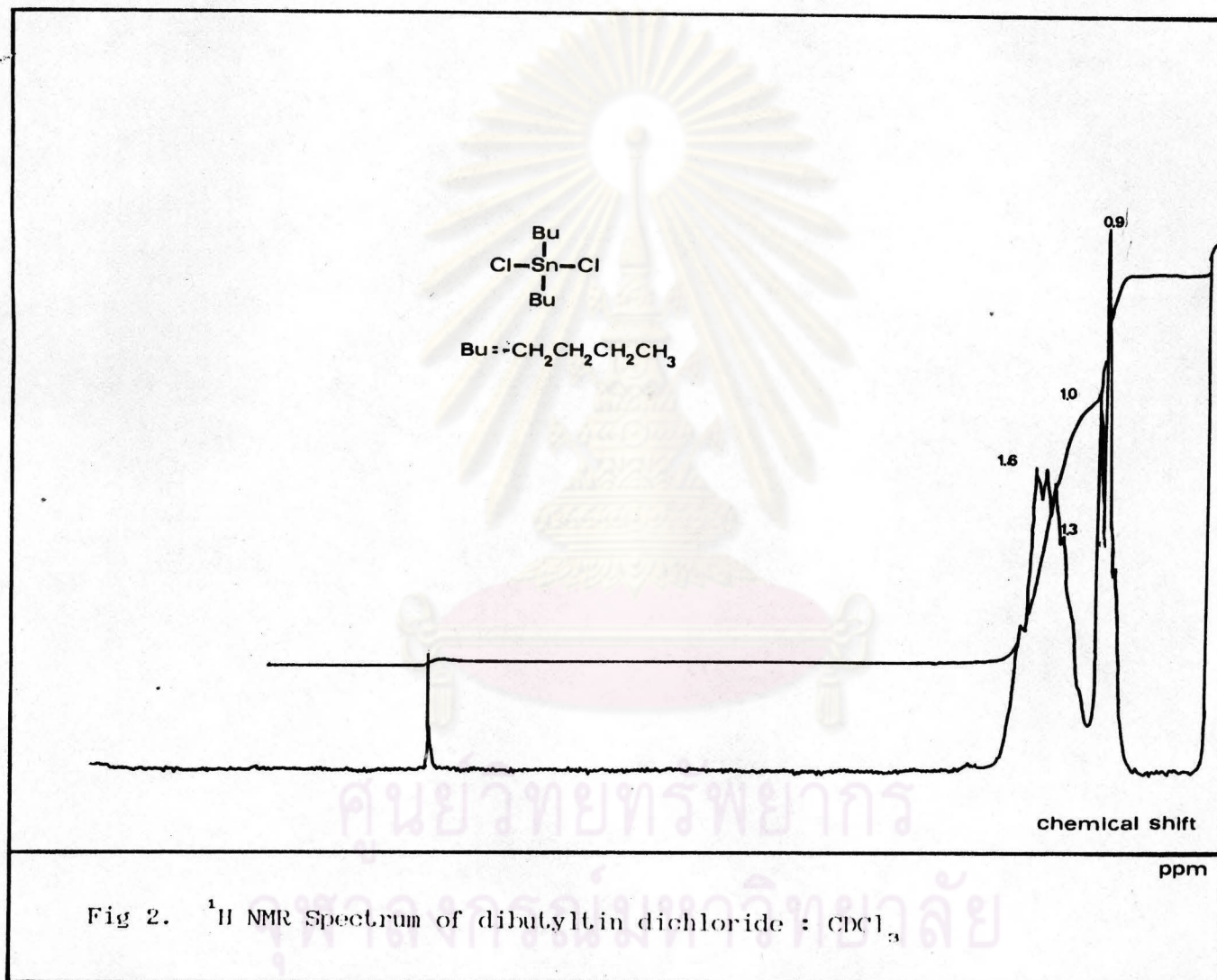
The ^1H and ^{13}C NMR spectra of monomers and polymers were taken by using Fourier Transform NMR spectrometer, Jeol, model JNX-FX 90 Q. The samples were dissolved as 5% solution in CDCl_3 or any suitable solvents as indicated.

2.6.3. Differential Thermal analysis (DTA)

DTA thermograms of polymers were obtained over the temperature range 40 to 400°C with the heating rate $10^\circ\text{C}/\text{min}$, the $\text{N}_2(\text{g})$ flow rate 30 ml/min and the sensitivity setting of and were used. The weight of specimens used was mg. To obtain reliable T_g , T_m and T_c of the polymers.

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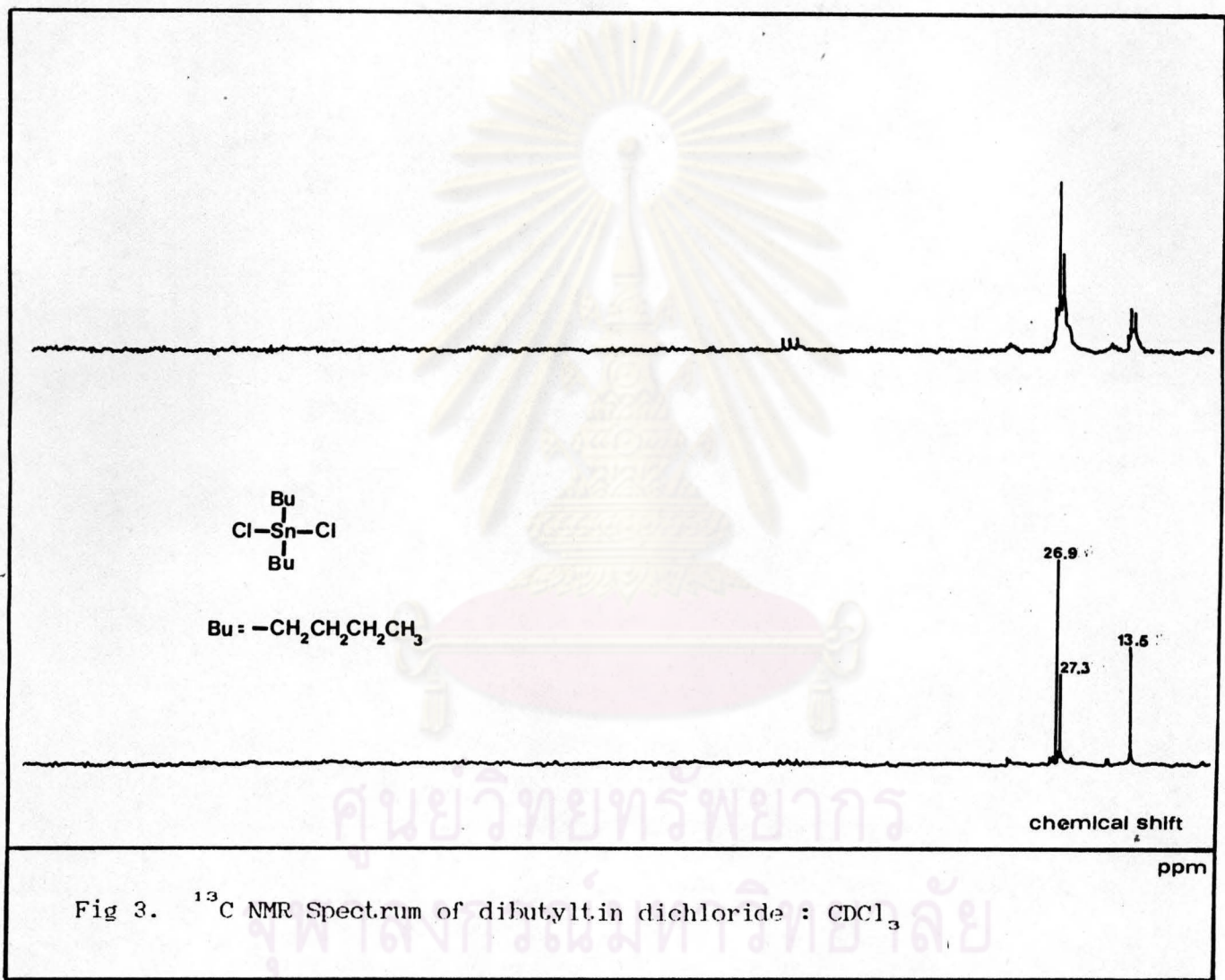


Fig 3. ¹³C NMR Spectrum of dibutyltin dichloride : CDCl₃

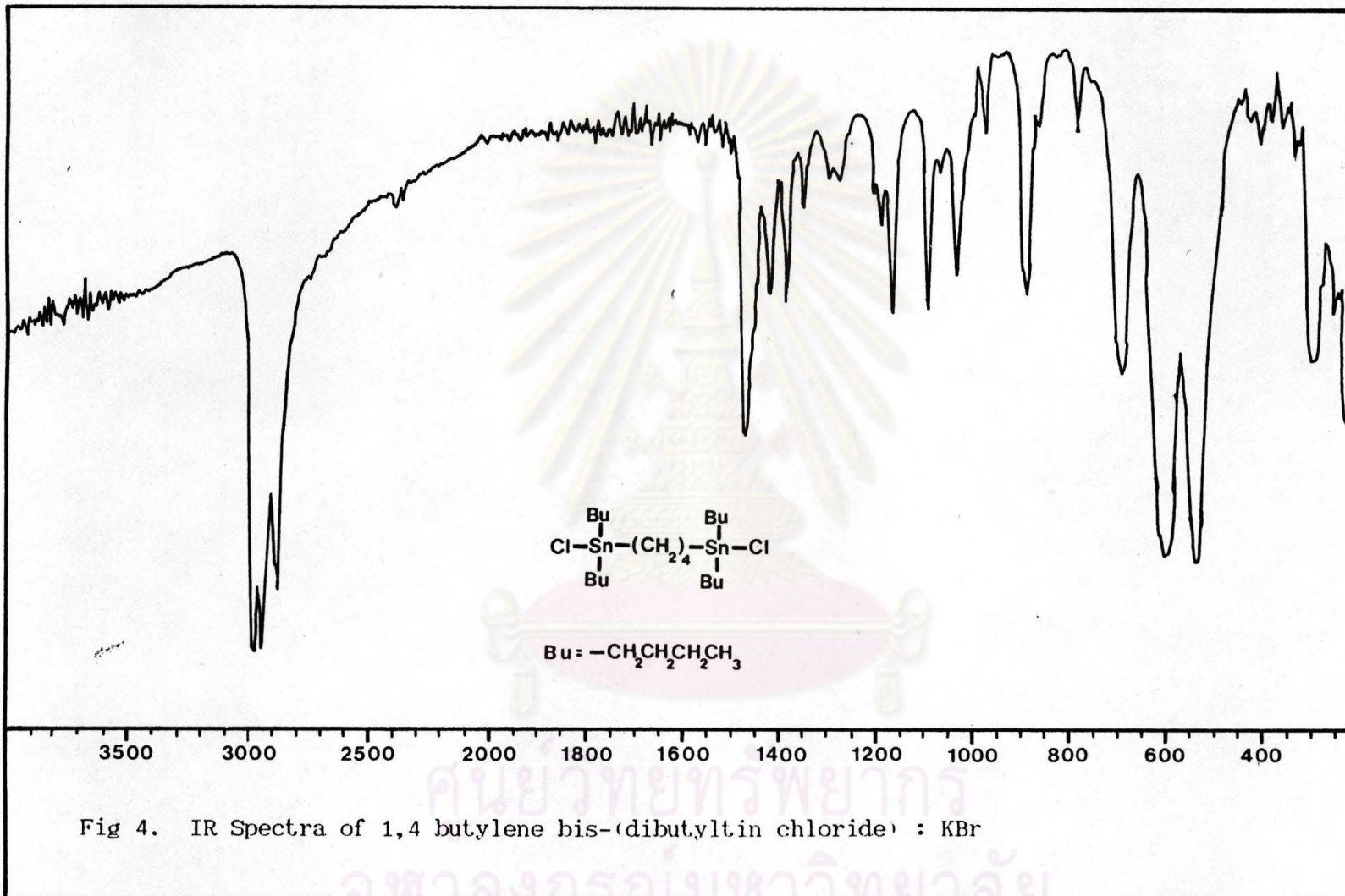
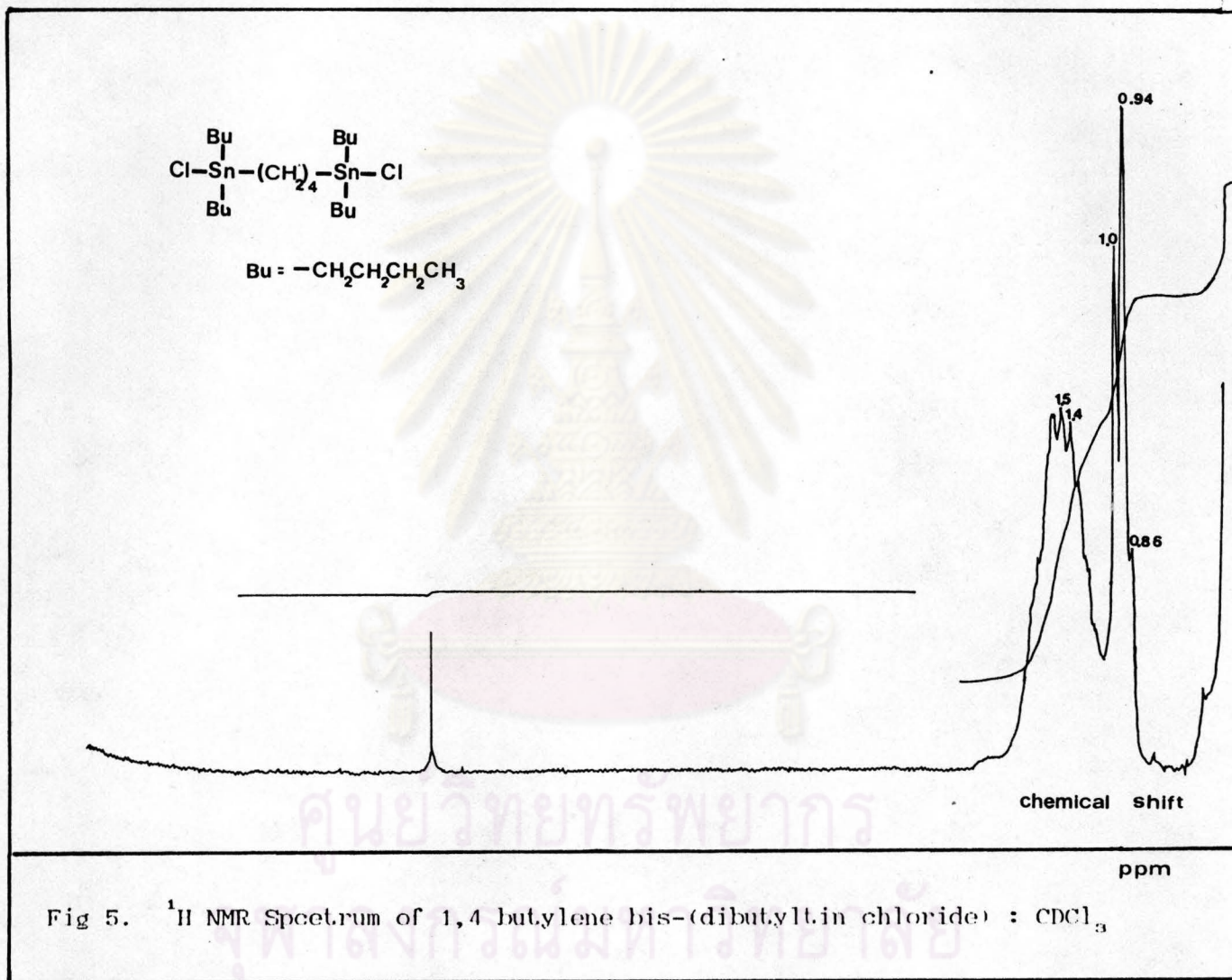
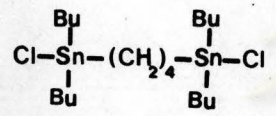


Fig 4. IR Spectra of 1,4 butylene bis-(dibutyltin chloride) : KBr





Bu: $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$

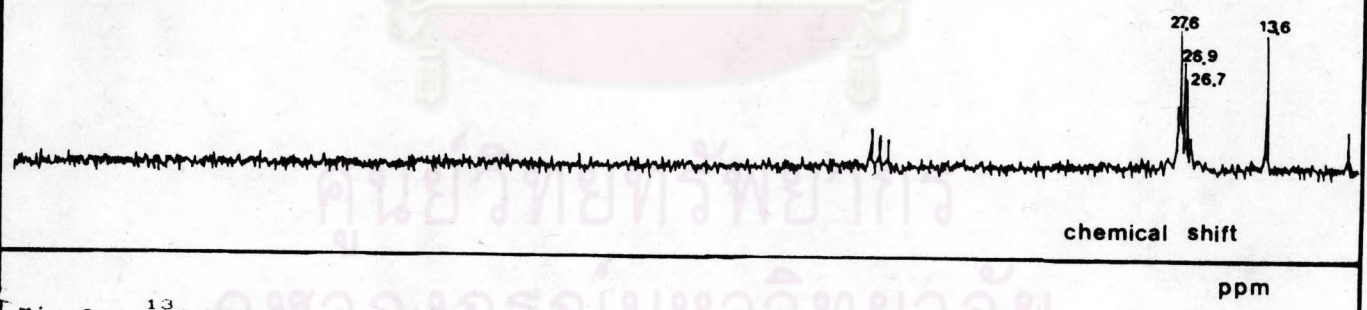


Fig 6. ^{13}C NMR Spectrum of 1,4 butylene bis-(dibutyltin chloride) : CDCl_3

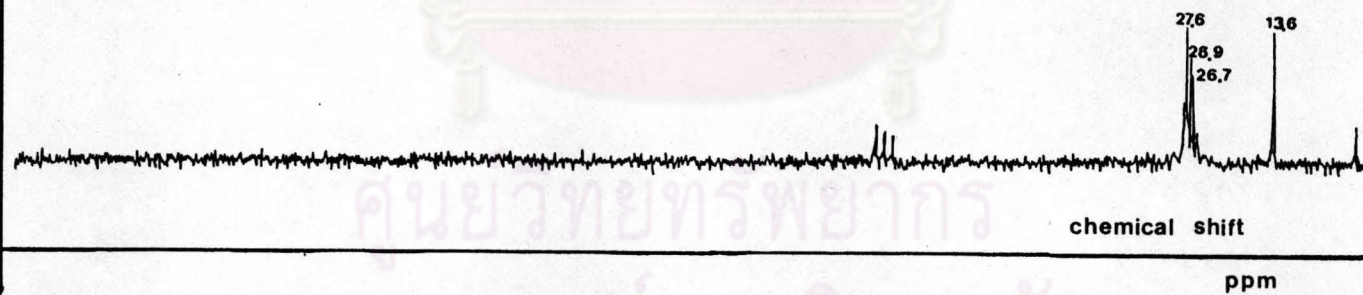
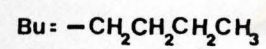
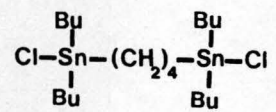


Fig 6. ^{13}C NMR Spectrum of 1,4 butylene bis-(dibutyltin chloride) : CDCl_3

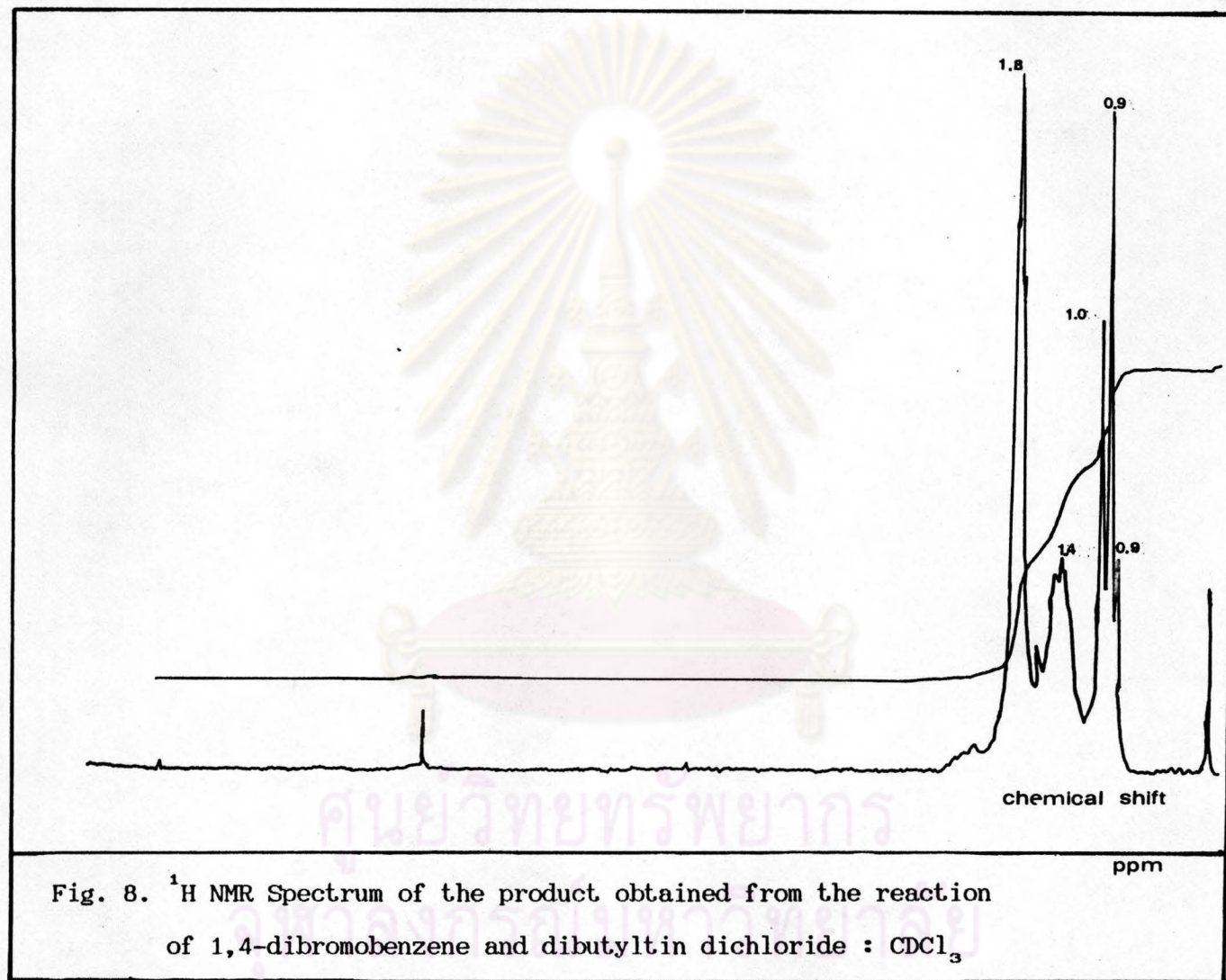


Fig. 8. ^1H NMR Spectrum of the product obtained from the reaction of 1,4-dibromobenzene and dibutyltin dichloride : CDCl_3

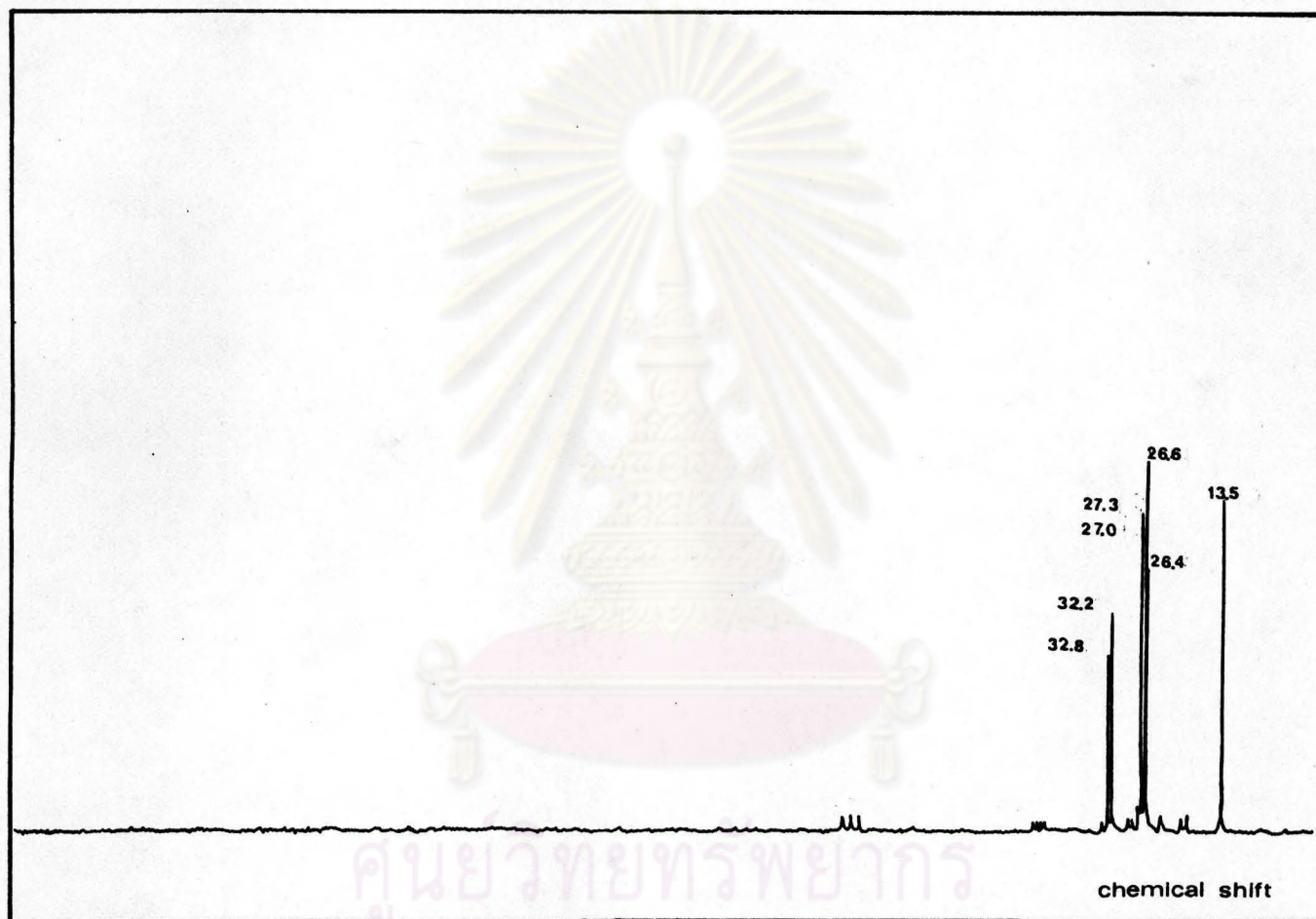
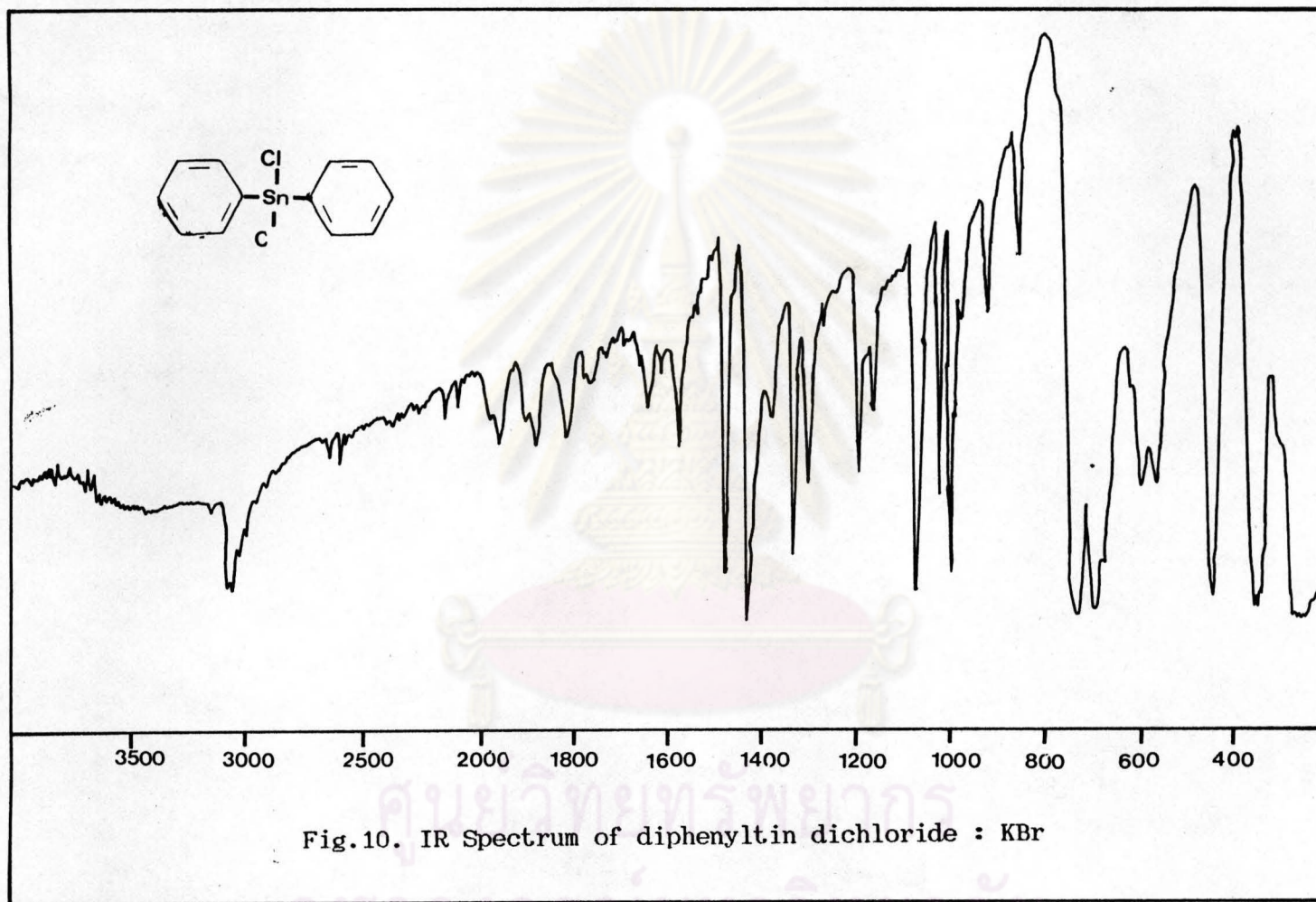


Fig. 9. ^{13}C NMR Spectrum of the product obtained from the reaction of 1,4-dibromobenzene and dibutyltin dichloride : CDCl_3 ppm



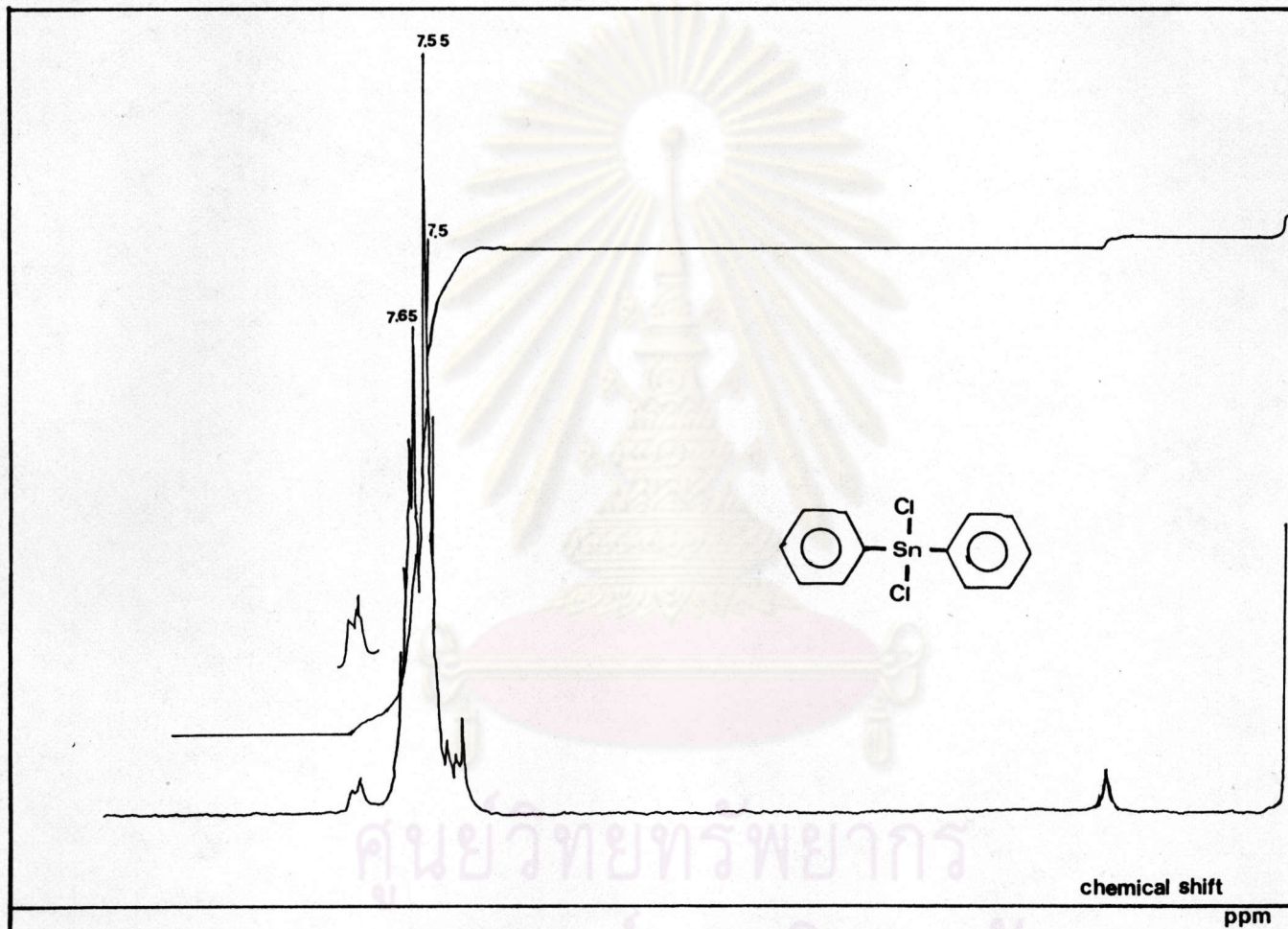
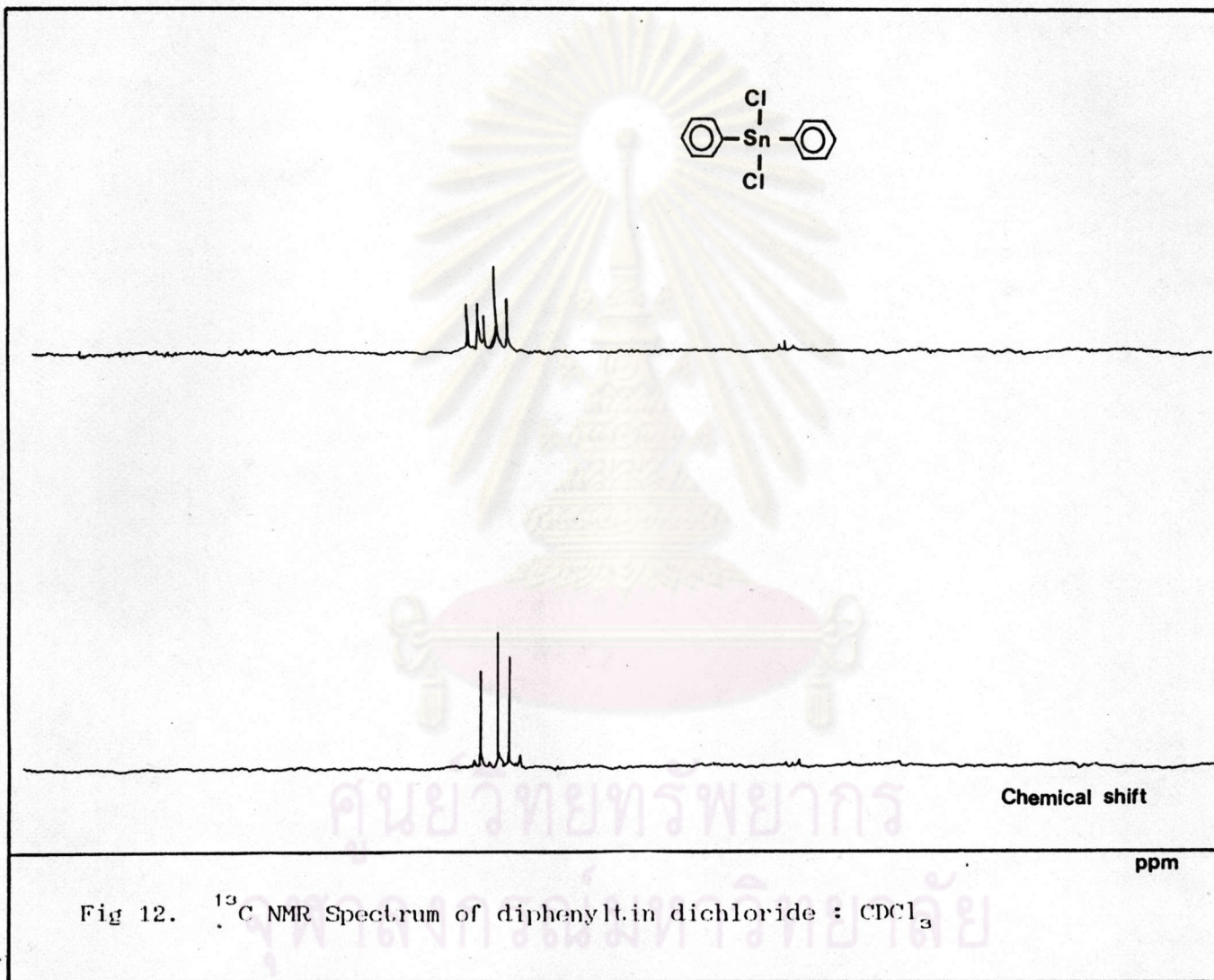


Fig.11. ^1H NMR Spectrum of diphenyltin dichloride : CDCl_3



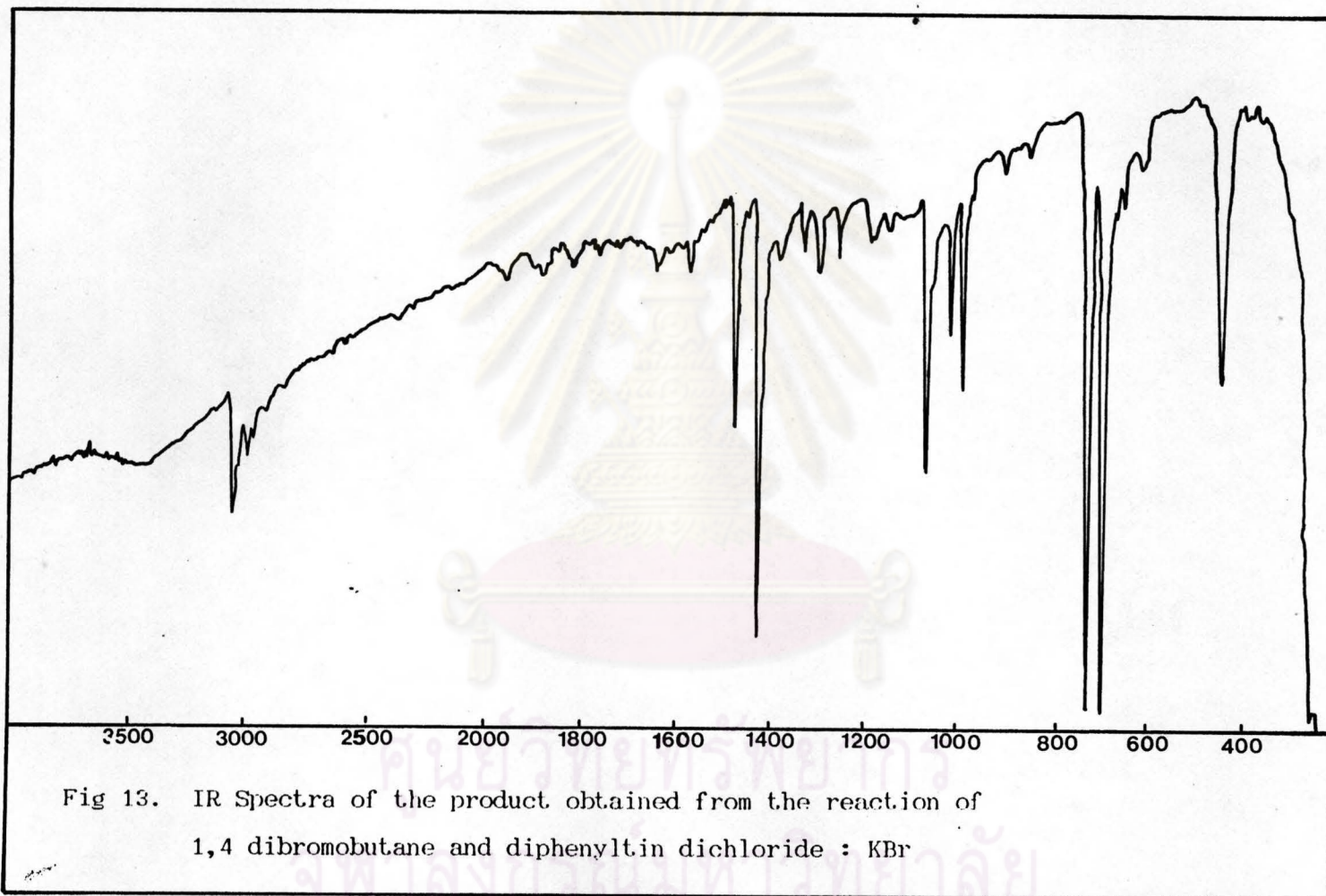


Fig 13. IR Spectra of the product obtained from the reaction of
1,4 dibromobutane and diphenyltin dichloride : KBr

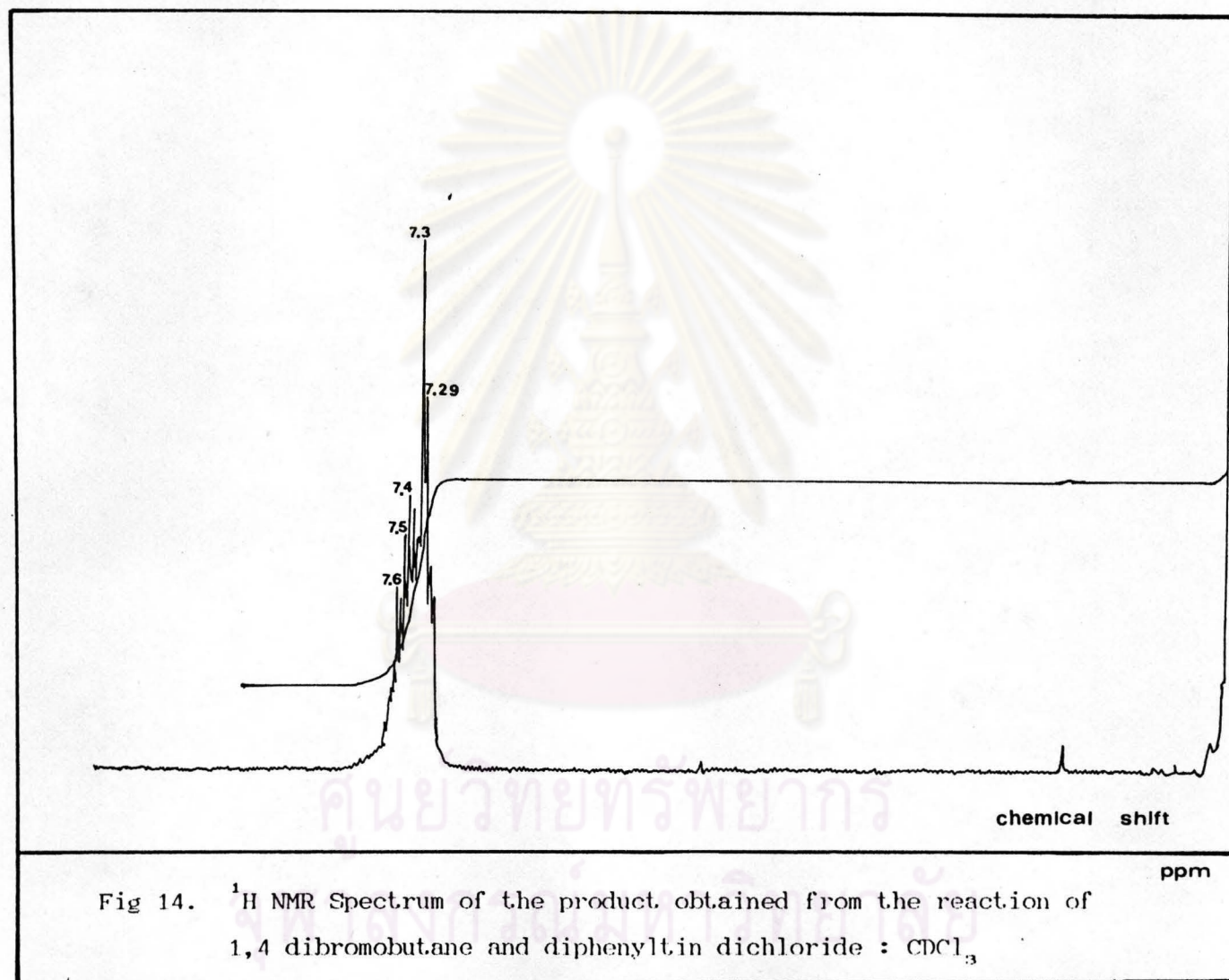


Fig 14. ^1H NMR Spectrum of the product obtained from the reaction of 1,4 dibromobutane and diphenyltin dichloride : CDCl_3

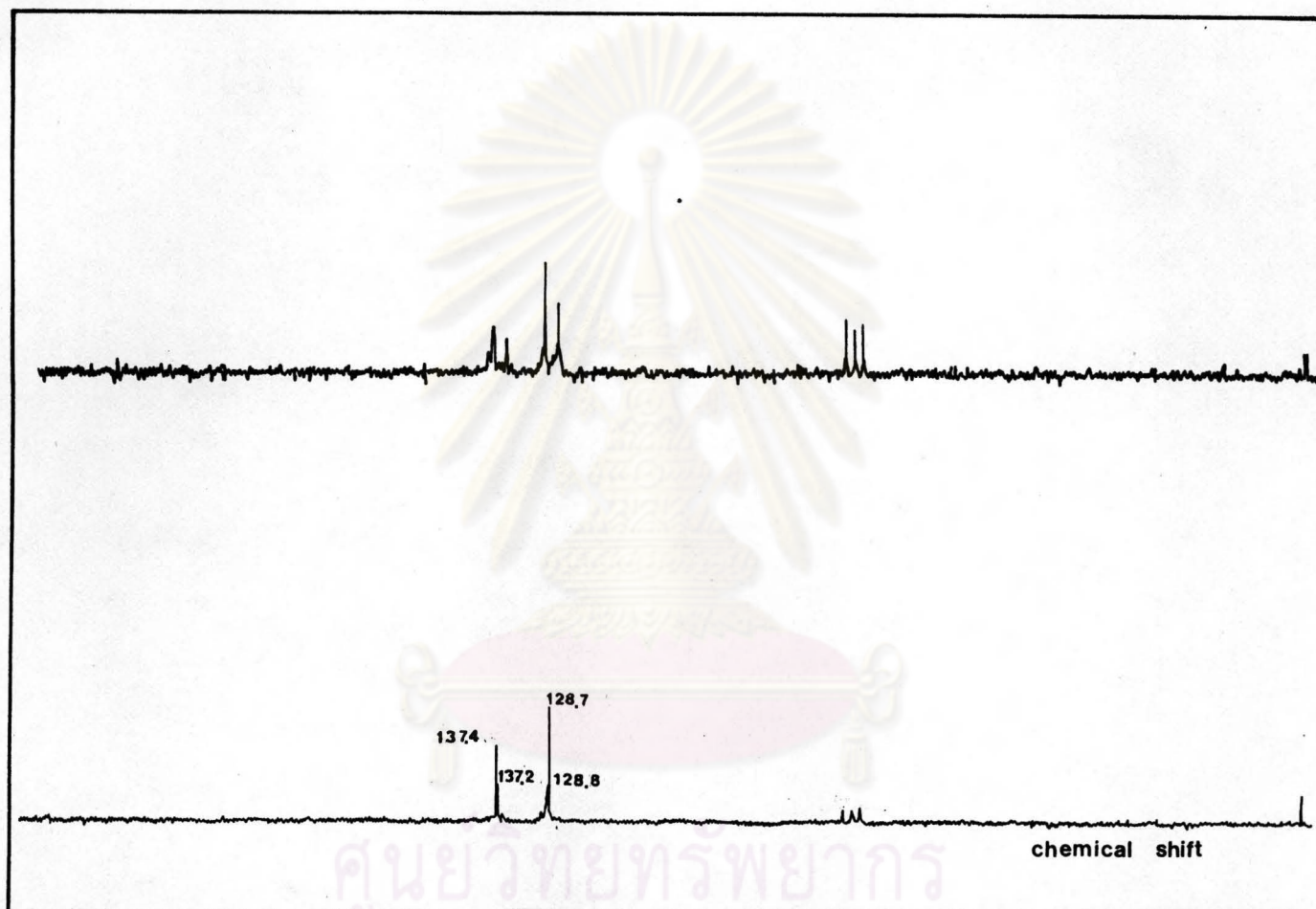
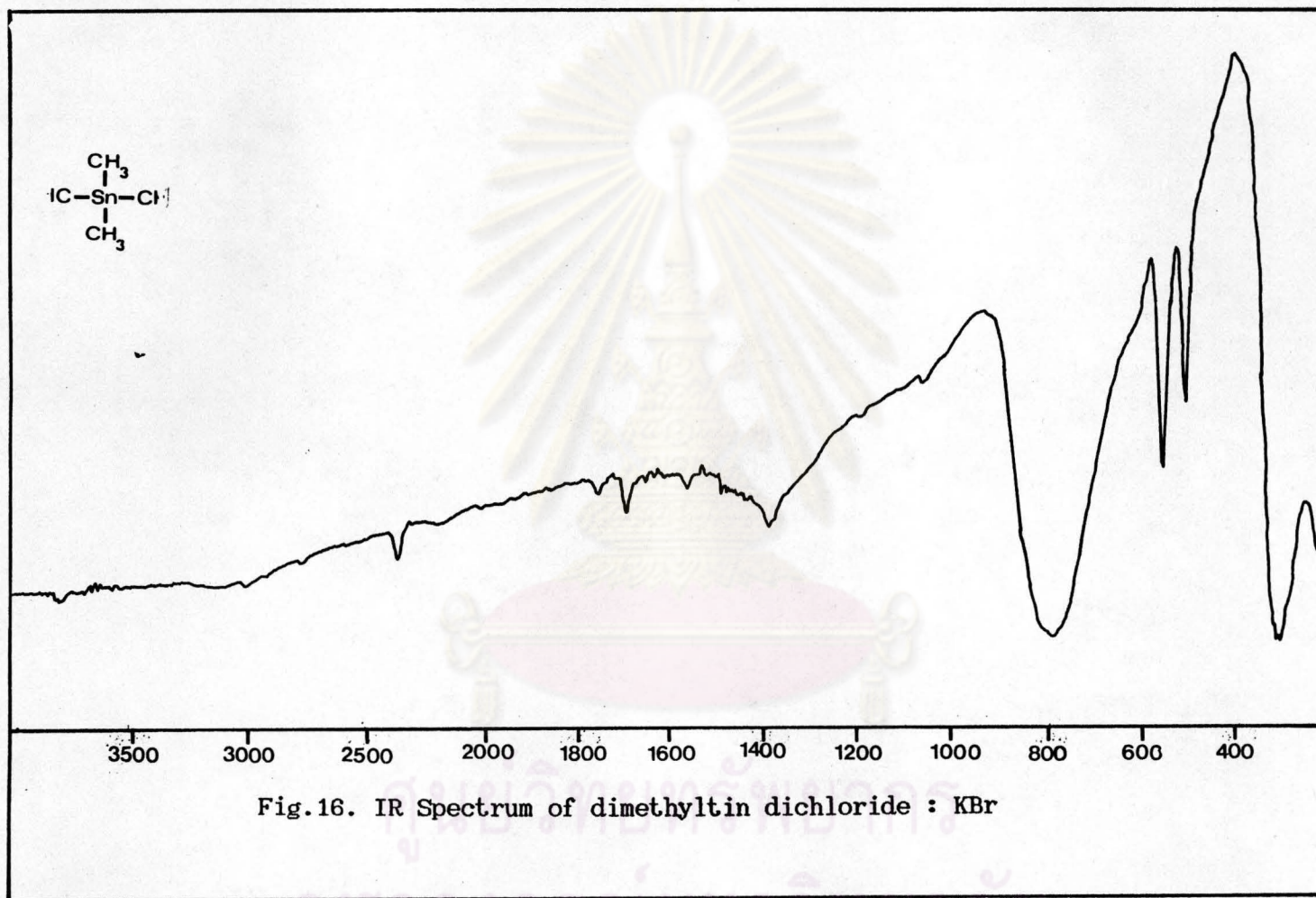
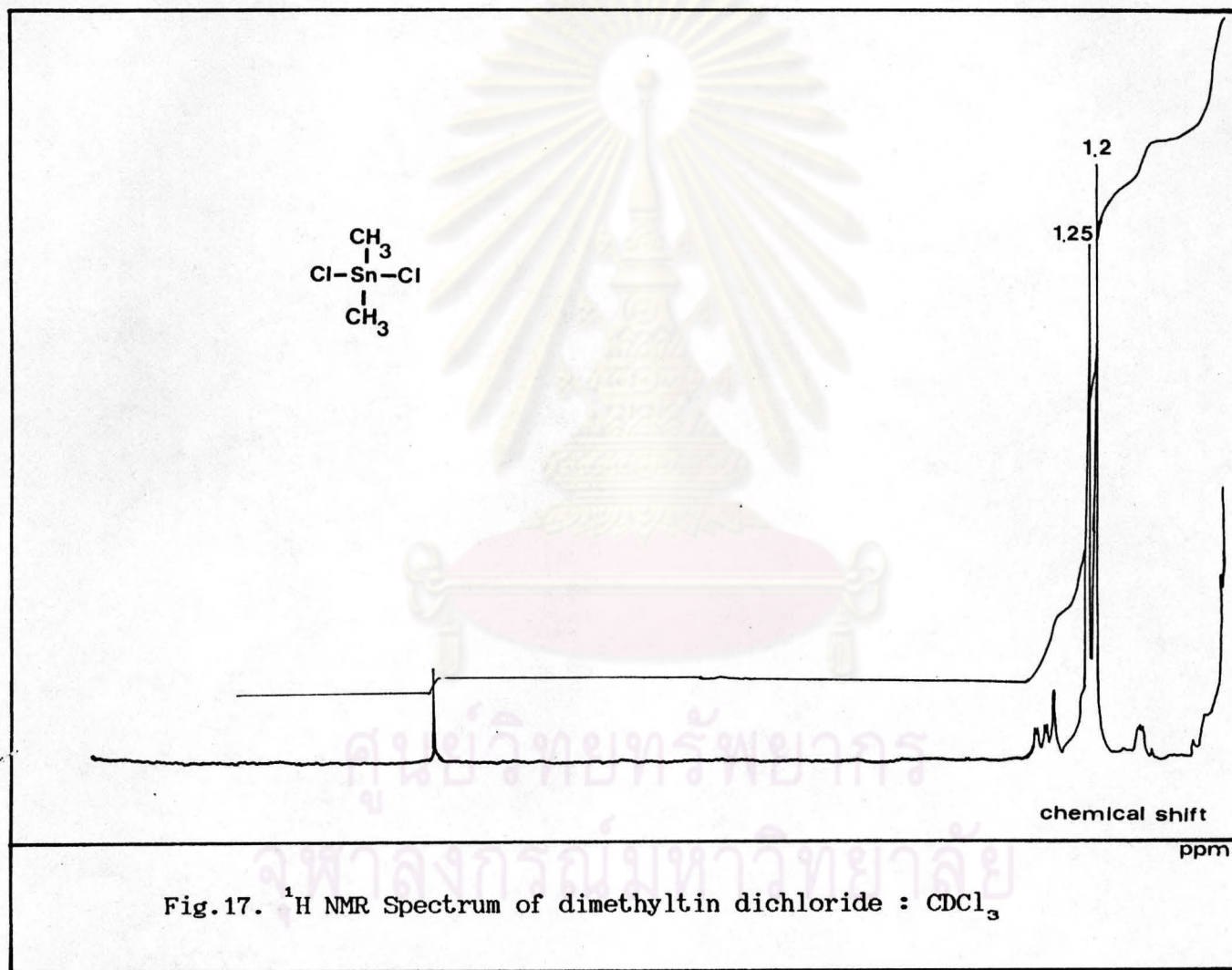


Fig.15. ^{13}C NMR Spectrum of the product obtained from the reaction of 1,4-dibromobutane and diphenyltin dichloride : CDCl_3





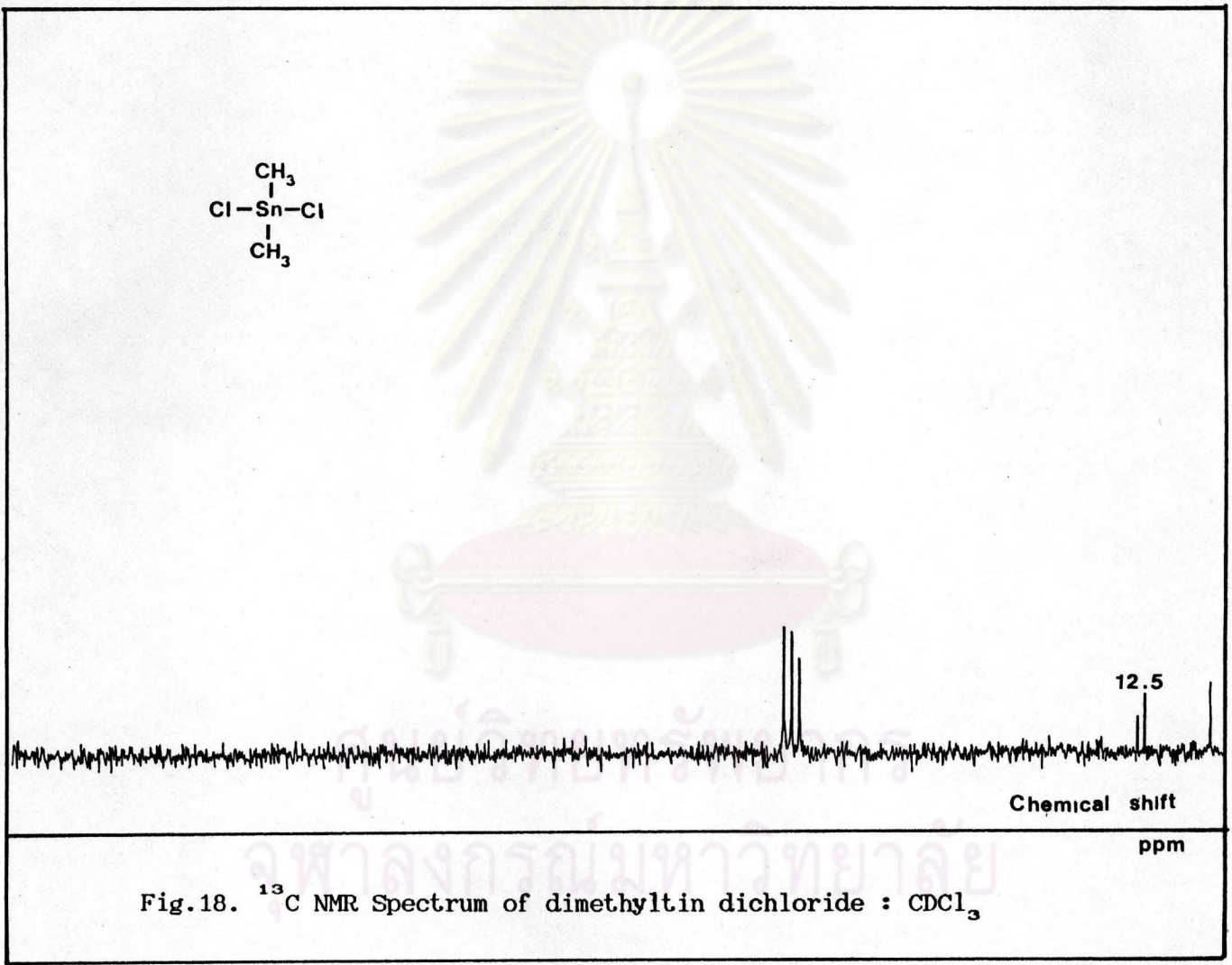
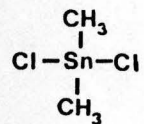
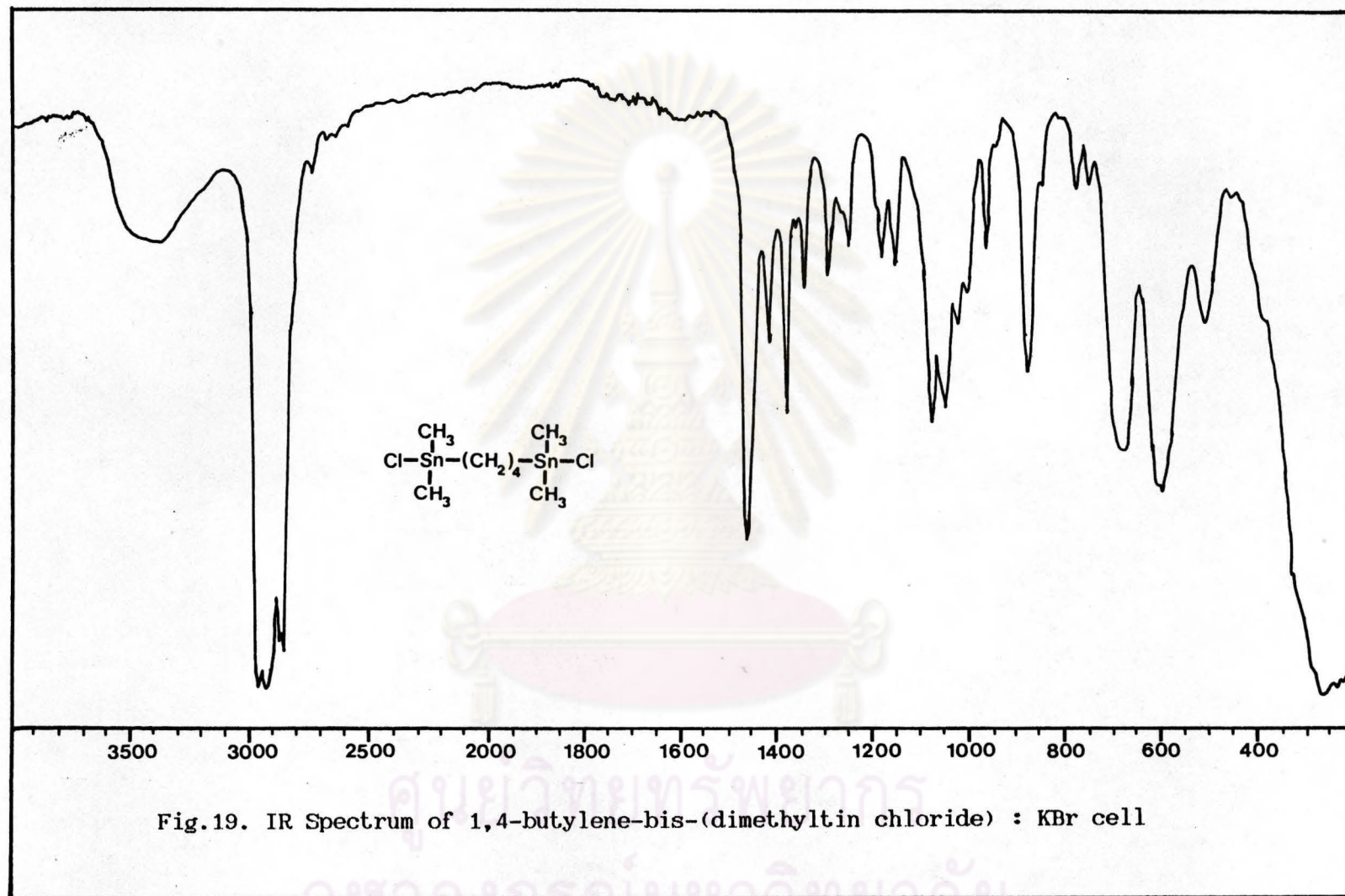


Fig.18. ^{13}C NMR Spectrum of dimethyltin dichloride : CDCl_3



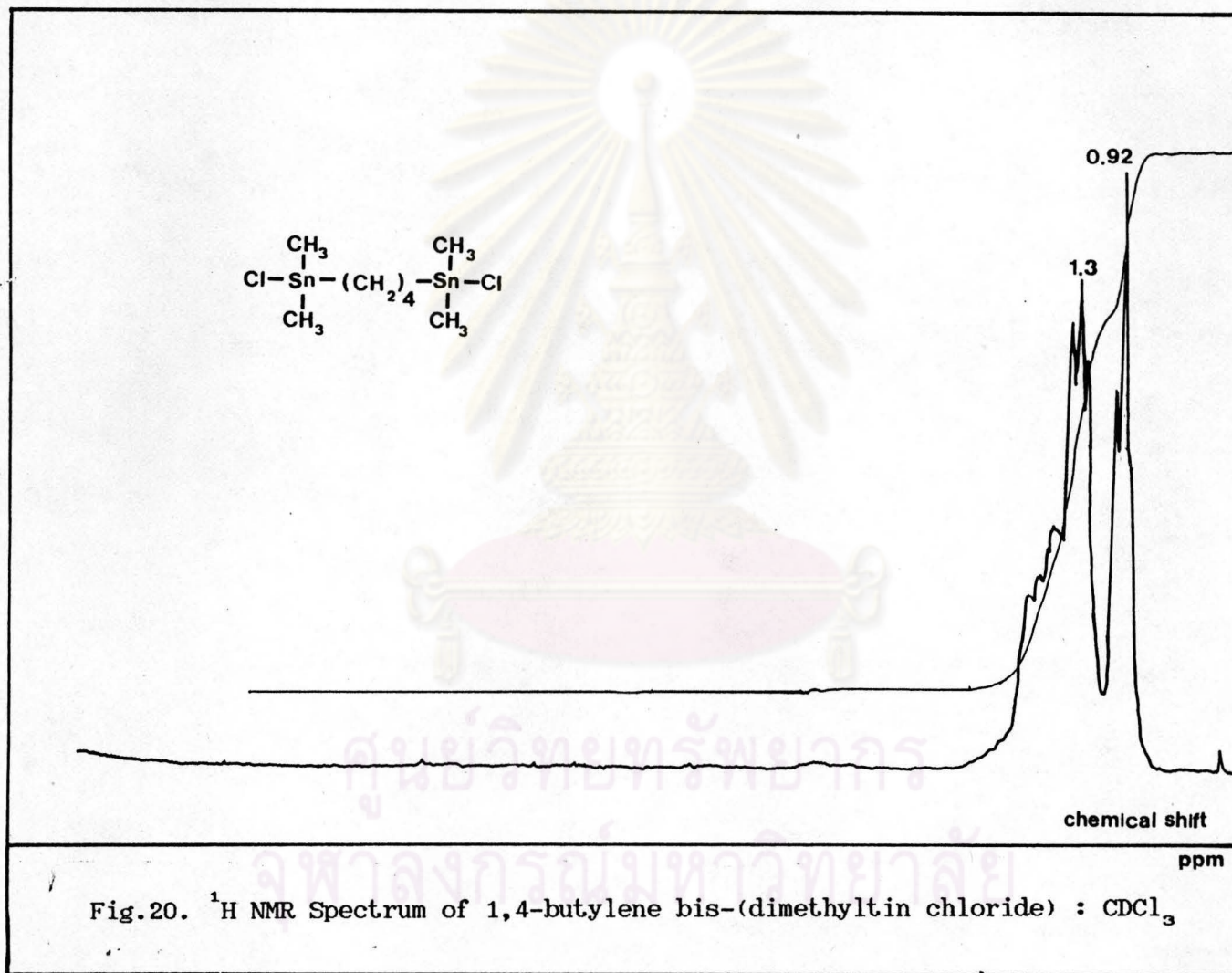
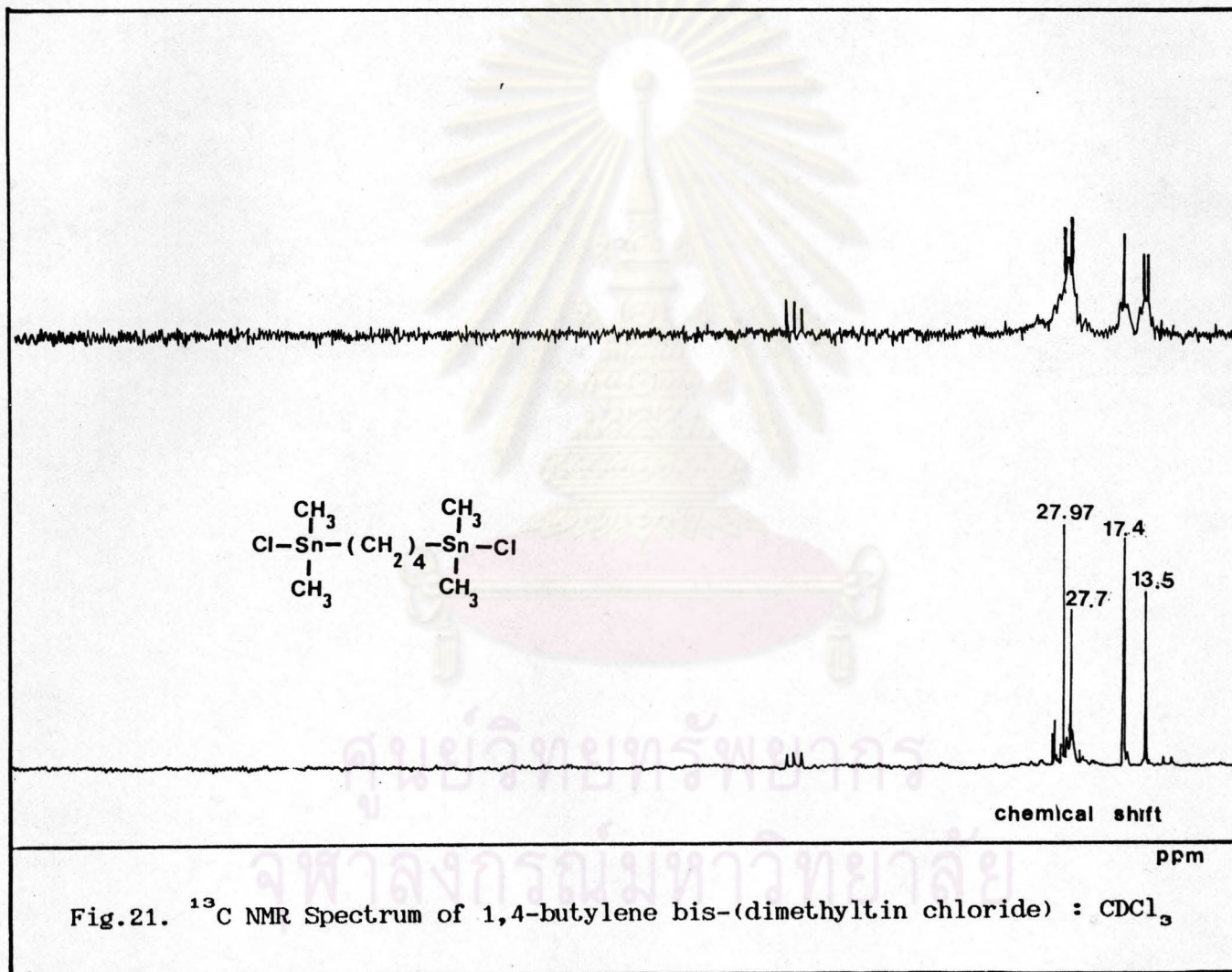


Fig.20. ¹H NMR Spectrum of 1,4-butylene bis-(dimethyltin chloride) : CDCl₃



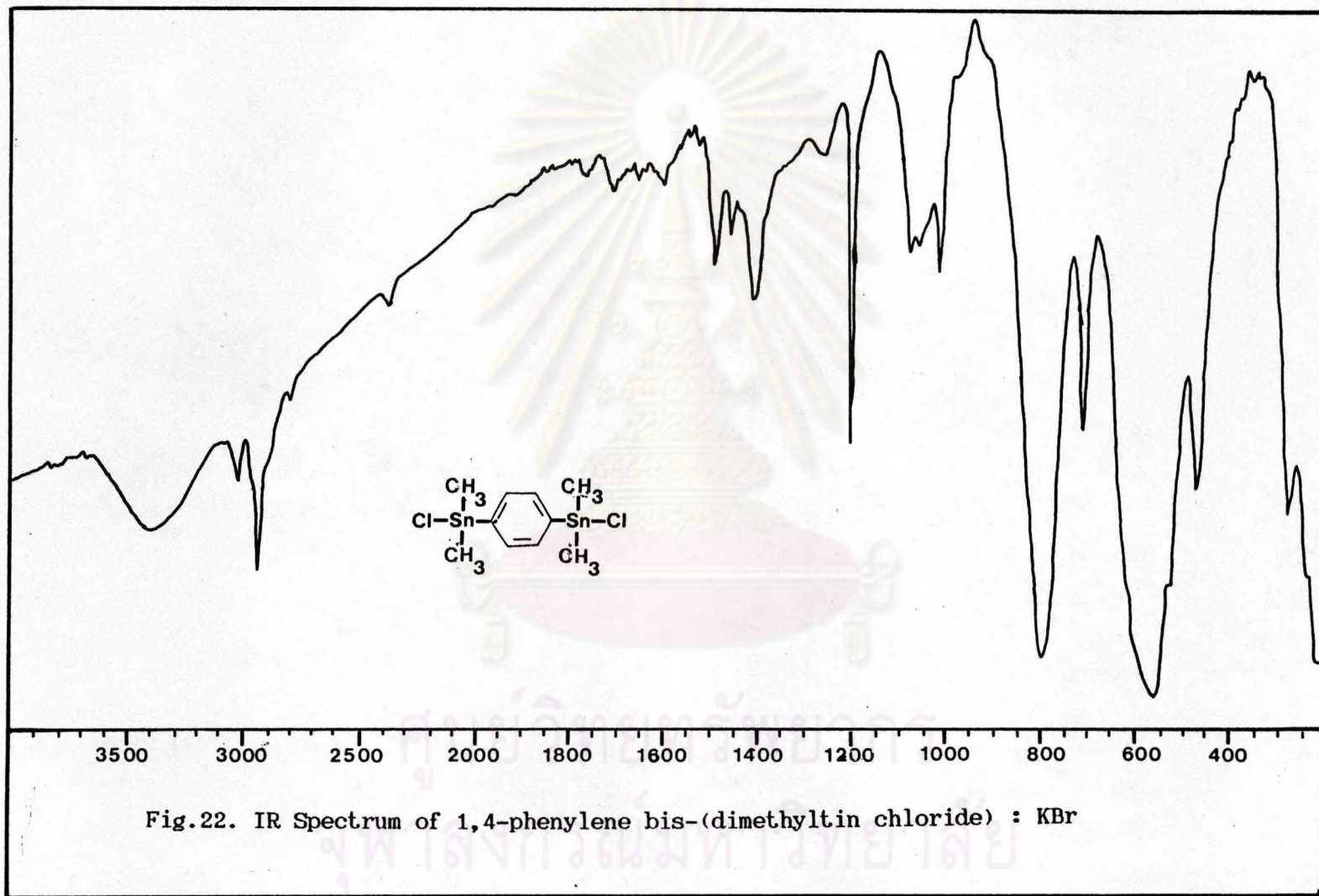
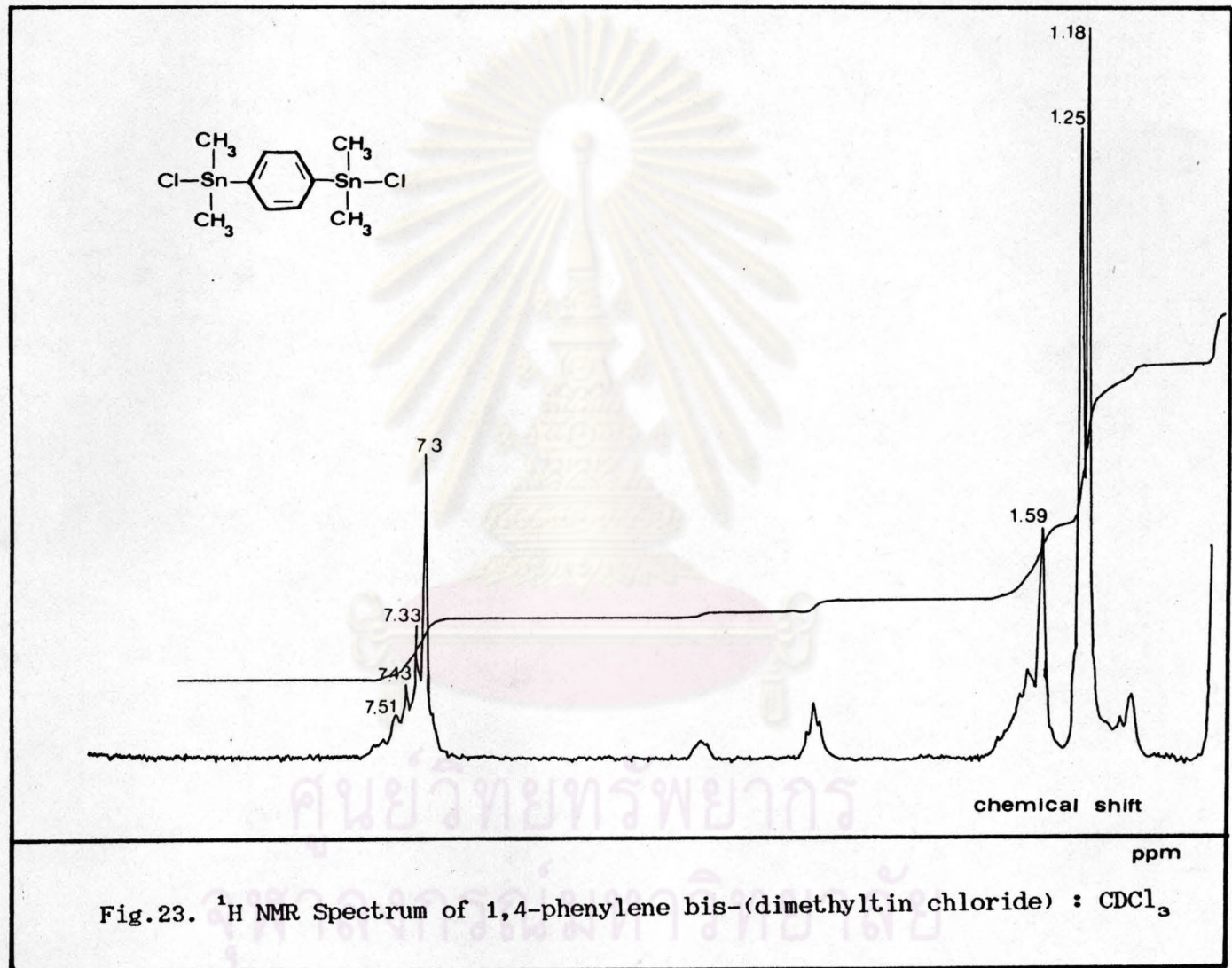


Fig.22. IR Spectrum of 1,4-phenylene bis-(dimethyltin chloride) : KBr



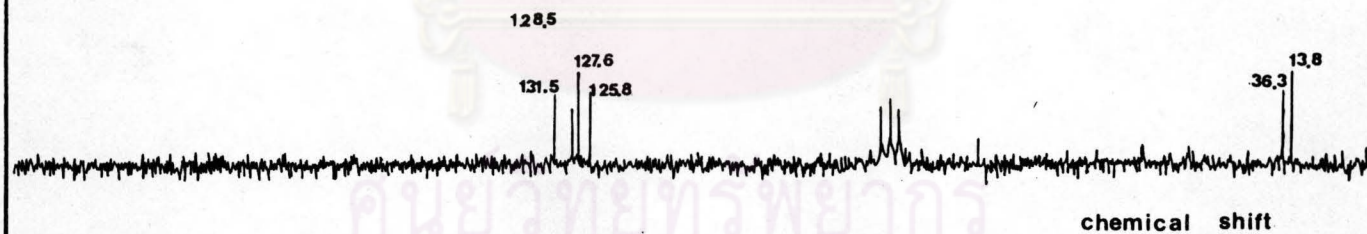
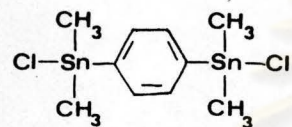


Fig.24. ^{13}C NMR Spectrum of 1,4-phenylene bis-(dimethyltin chloride) : CDCl_3 ppm

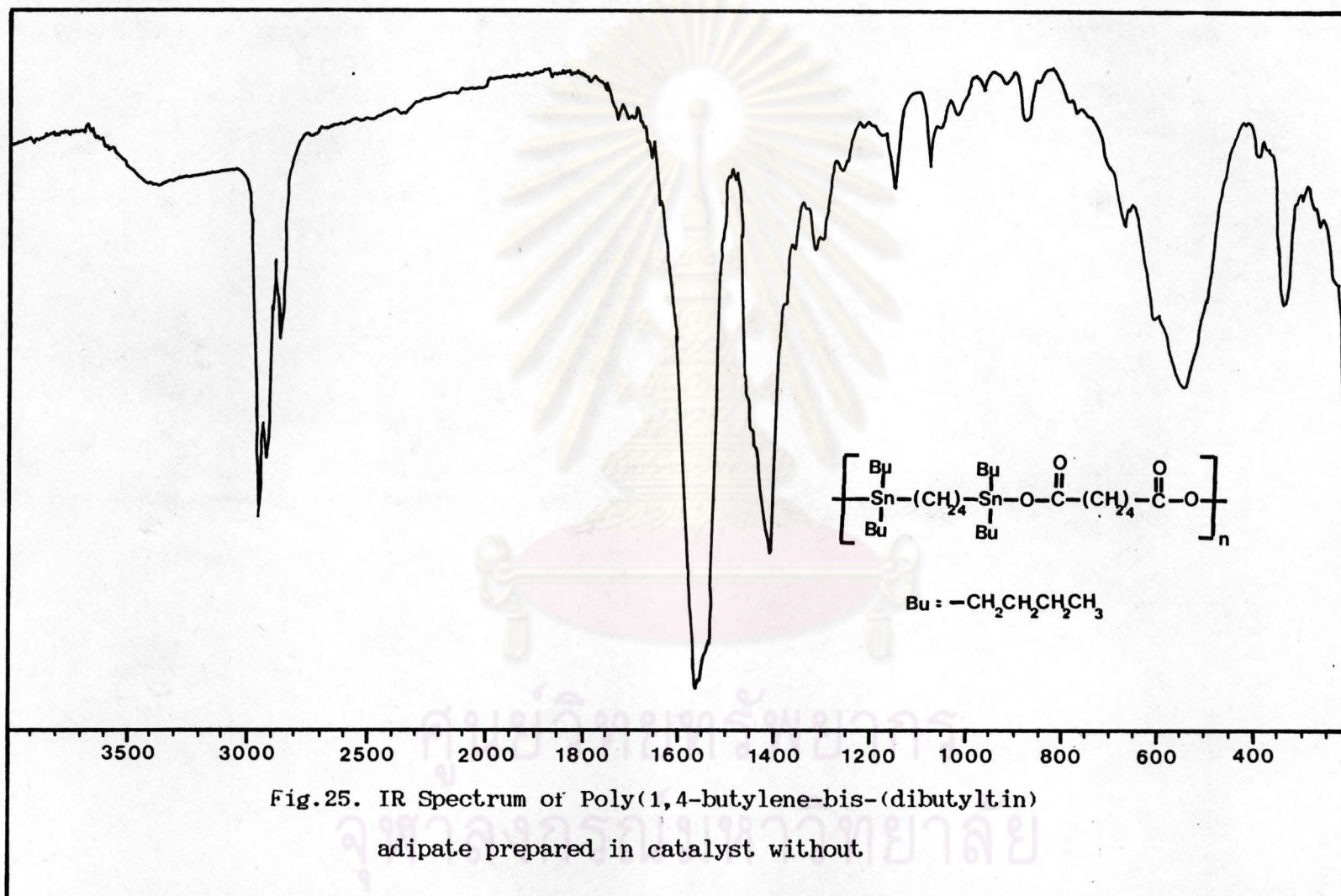
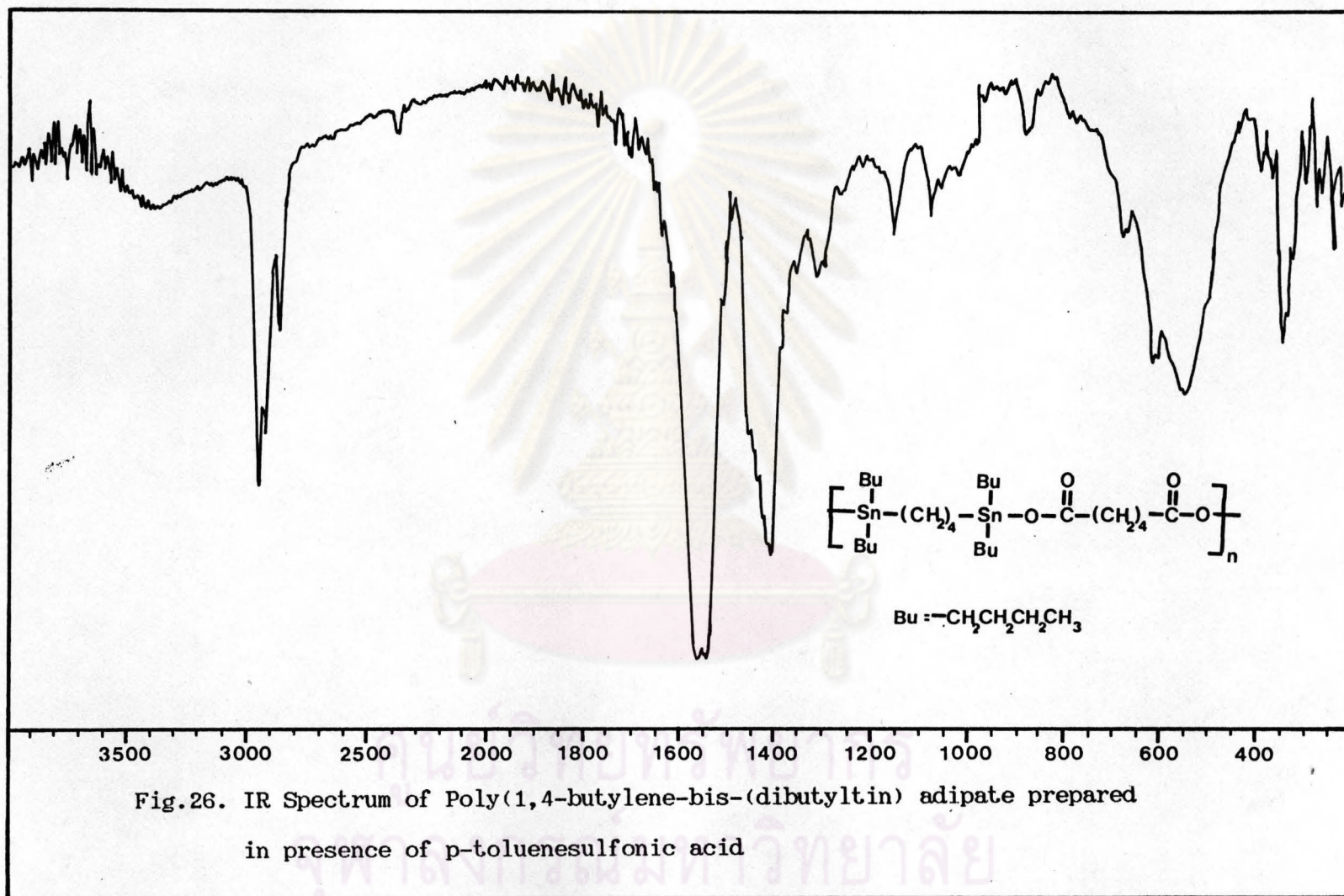
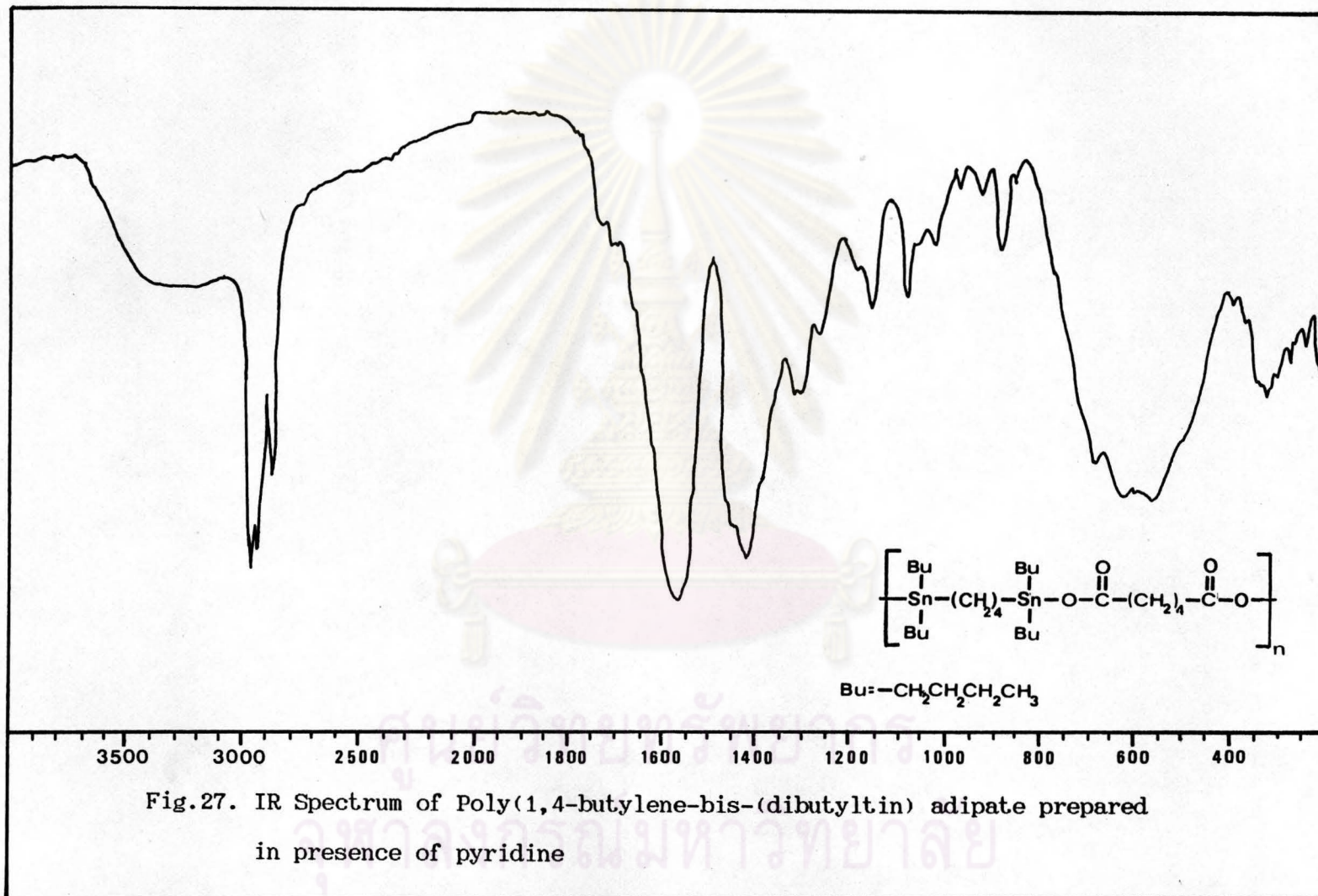
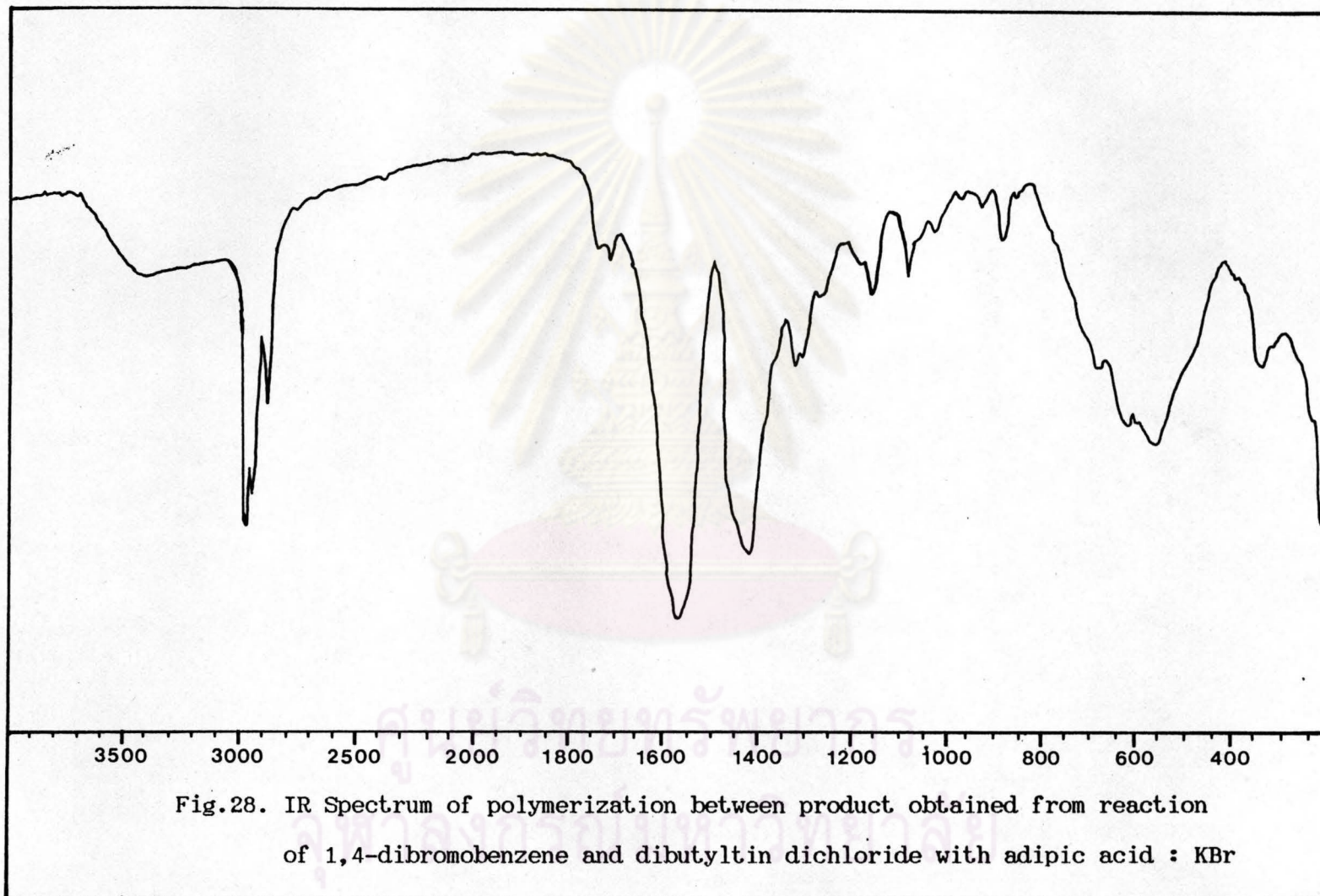
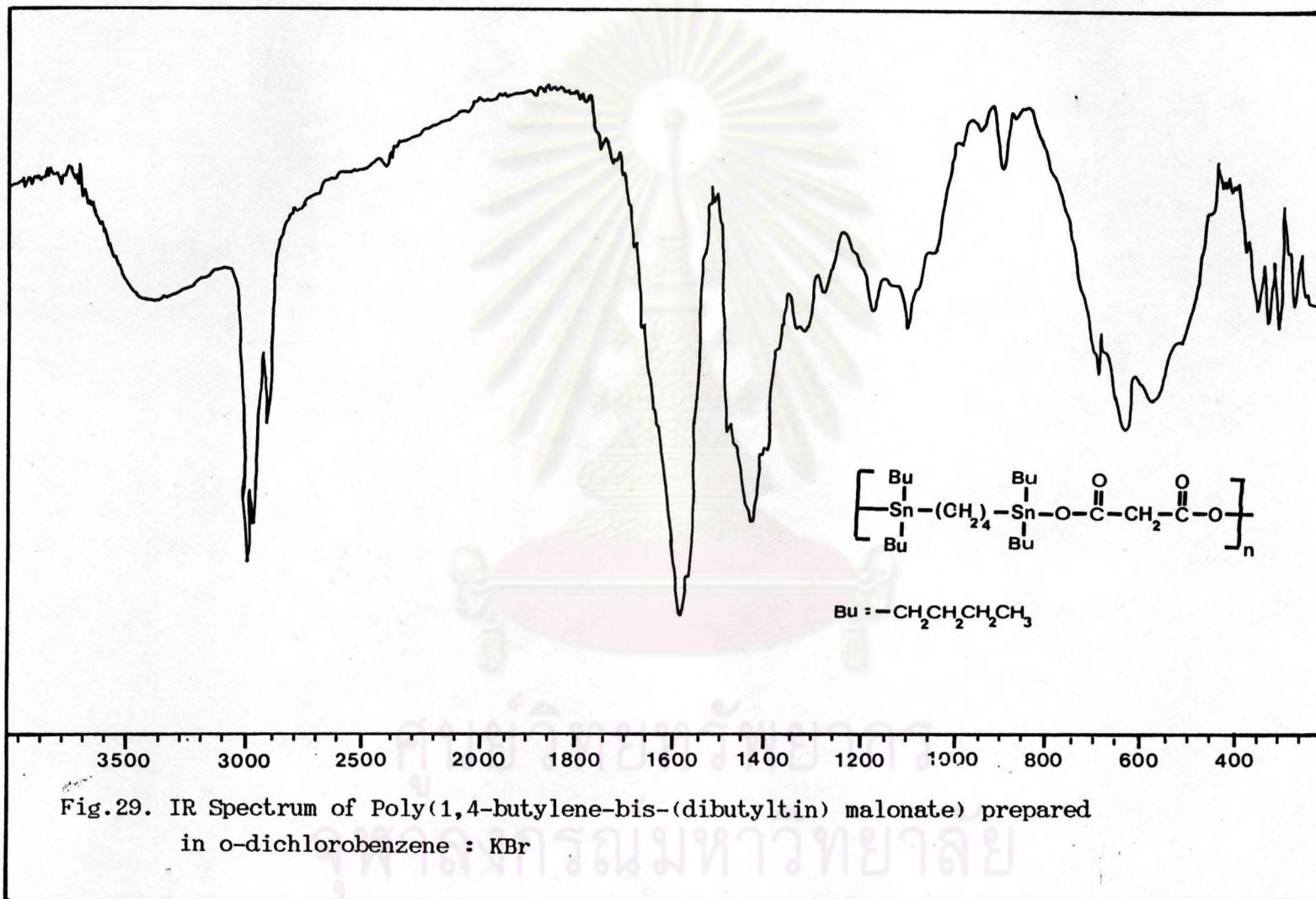


Fig.25. IR Spectrum of Poly(1,4-butylene-bis-(dibutyltin) adipate prepared in catalyst without









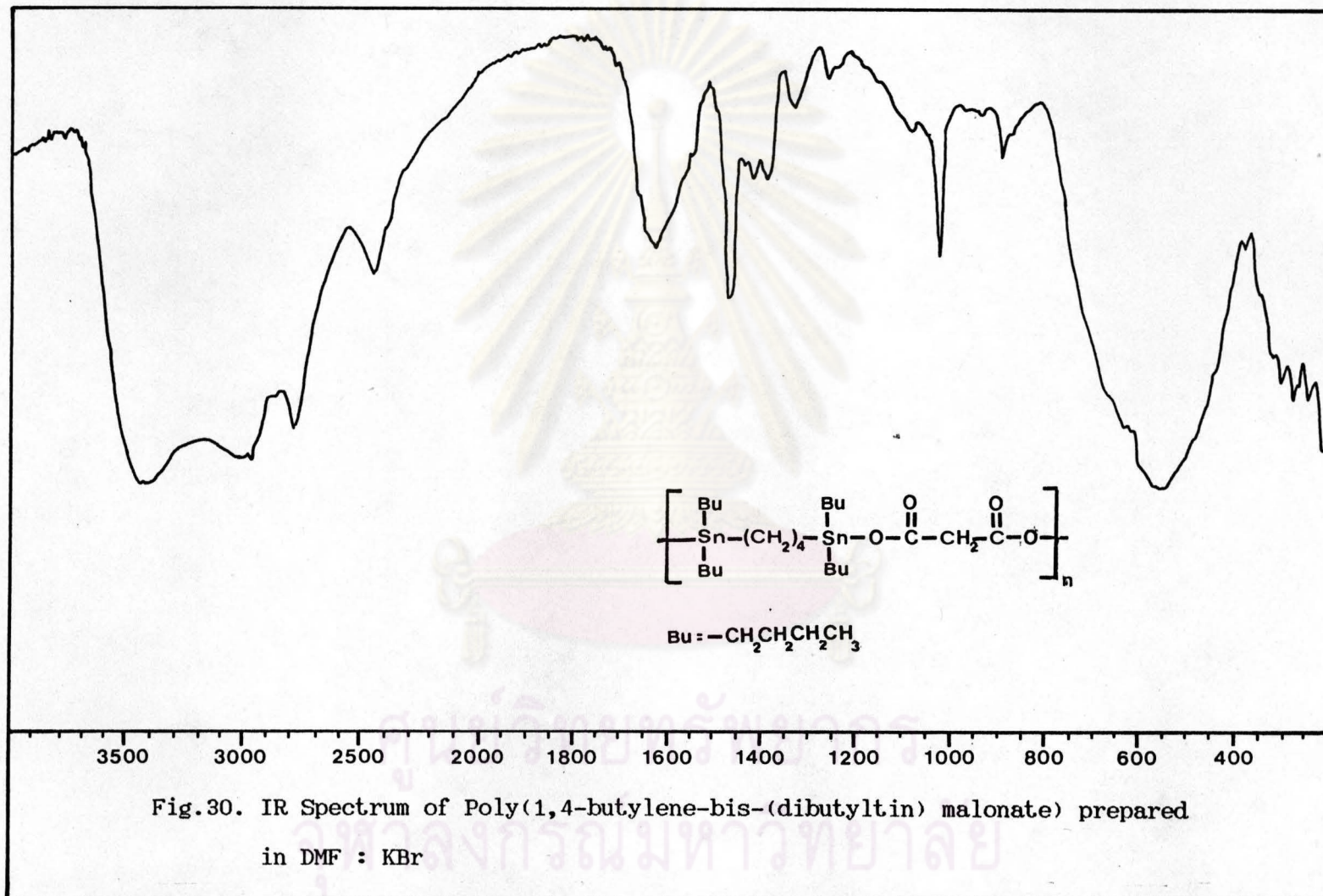


Table 5. Show % Sn in Poly(1,4-butylene-bis-(dibutyltin)adipate
by I.C.P.S.

Time	Sample	%Sn	Sample	%Sn	Sample	%Sn
10	W10 1:10	35.08	C101:1.0	35.35	P101:1.0	36.18
	W101:1.5	34.84	C101:1.5	36.01	P101:1.5	36.17
	W10 1:2	35.43	C101:2	35.39	P101:2	35.84
15	W15 1:10	36.13	C151:1.0	35.67	P151:1.0	35.69
	W15 1:1.5	35.12	C151:1.5	35.63	P151:1.5	36.18
	W15 1:2	36.06	C151:2	35.61	P151:1	35.49
20	W20 1:10	35.03	C201:1.0	35.48	P201:1.0	35.78
	W20 1:1.5	35.90	C201:1.5	36.08	P201:1.5	36.01
	W20 1:2	35.49	C201:2	35.35	P201:2	36.08

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Table 6. Show C, H, O, Sn of Poly(1,4-butylene-bis-(dibutyltin) adipate prepared without catalyst

Time	Sample No.	C	H	O	Sn
10	W10 1:10	46.92	7.84	10.16	35.08
	W10 1:1.5	46.78	7.76	10.62	34.84
	W10 1:2	46.89	7.52	10.51	35.43
15	W15 1:10	46.18	7.56	10.13	36.13
	W15 1:1.5	46.97	7.57	10.34	35.12
	W15 1:2	46.81	7.89	9.24	36.06
20	W20 1:10	46.98	7.81	10.18	35.03
	W20 1:1.5	46.90	7.82	9.38	35.90
	W20 1:2	46.12	7.80	10.59	35.49

Note Theoretical calculation based on the following formular

Table 7. Show C, H, O, Sn of Poly(1,4-butylene-bis-(dibutyltin adipate) in presence of p-toluenesulfonic acid

Time	Sample No.	C	H	O	Sn
10	C10 1:10	46.15	7.75	10.75	35.35
	C10 1:1.5	46.18	7.81	10.00	34.01
	C10 1:2	47.32	7.82	10.47	35.39
15	C15 1:10	47.28	7.75	10.63	36.34
	C15 1:1.5	47.12	7.72	10.13	35.03
	C15 1:2	47.07	7.84	9.08	36.01
20	C20 1:10	46.92	7.79	10.11	35.18
	C20 1:1.5	46.32	7.80	9.70	35.18
	C20 1:2	47.00	7.81	10.84	35.35

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Table 8. Show C, H, O, Sn of Poly(1,4-butylene-bis-(dibutyltin adipate) in presence of pyridine

Time	Sample No.	C	H	O	Sn
10	P10 1:10	46.35	7.72	9.75	36.18
	P10 1:1.5	46.84	7.70	9.29	36.17
	P10 1:2	46.89	7.74	10.58	34.79
15	P15 1:10	46.86	7.79	10.16	35.19
	P15 1:1.5	46.42	7.81	8.59	37.18
	P15 1:2	46.94	7.82	10.49	34.75
20	P20 1:10	46.72	7.84	8.43	37.01
	P20 1:1.5	46.54	7.87	11.15	34.44
	P20 1:2	46.82	7.89	9.21	36.08

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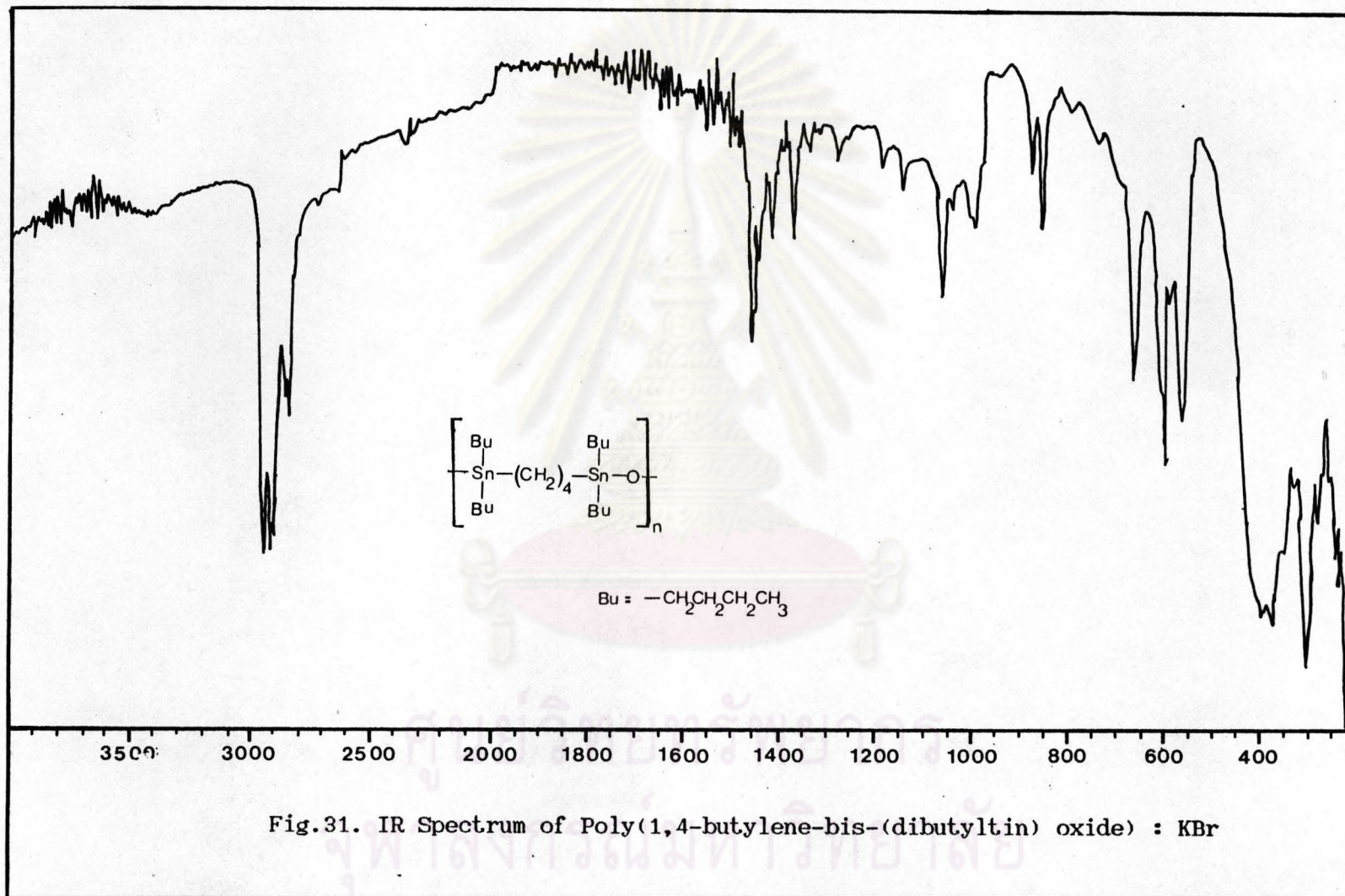


Fig.31. IR Spectrum of Poly(1,4-butylene-bis-(dibutyltin) oxide) : KBr

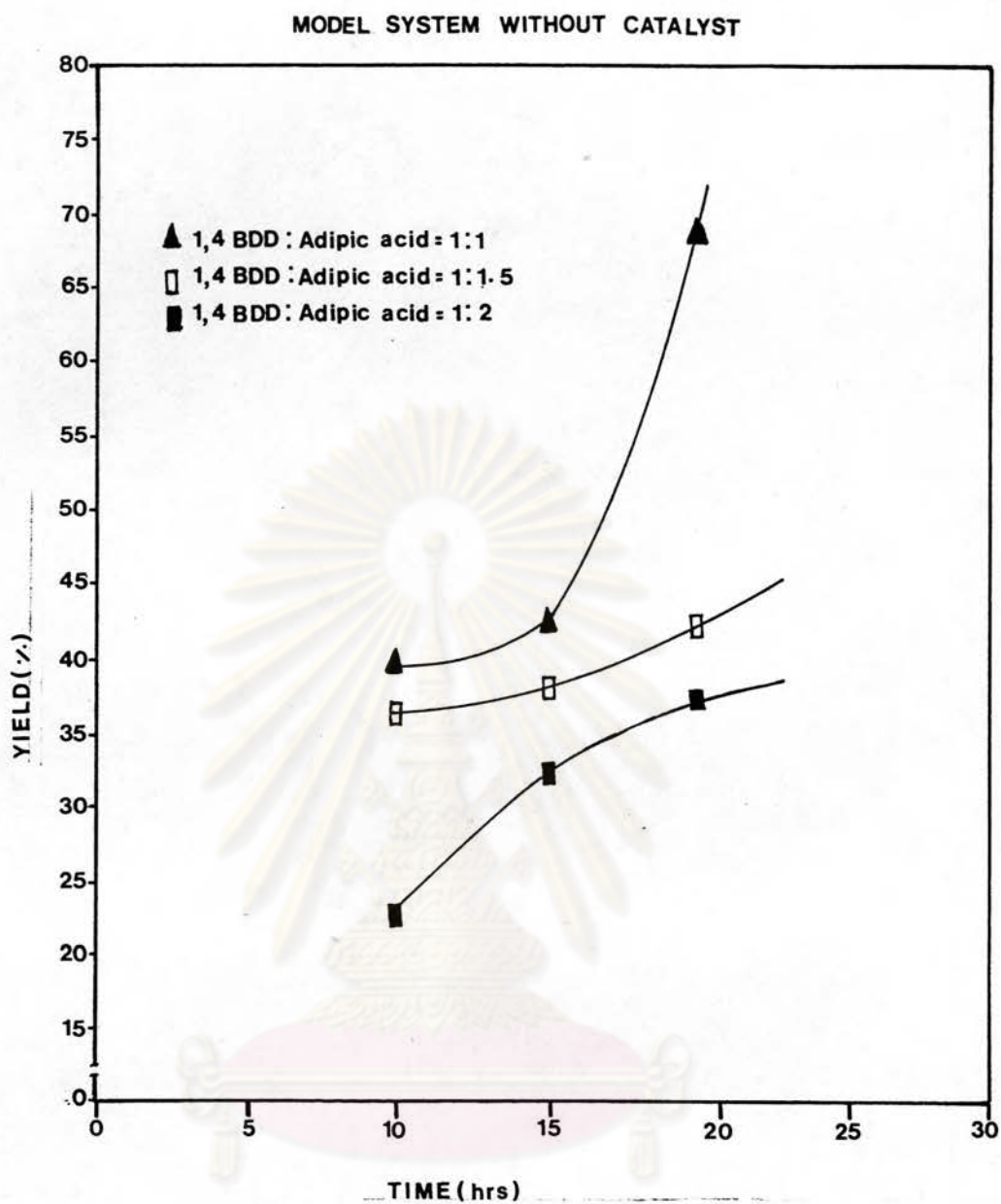


Fig.32. Graph of Poly(1,4-butylene-bis-(dibutyltin) adipate) prepared in without catalyst

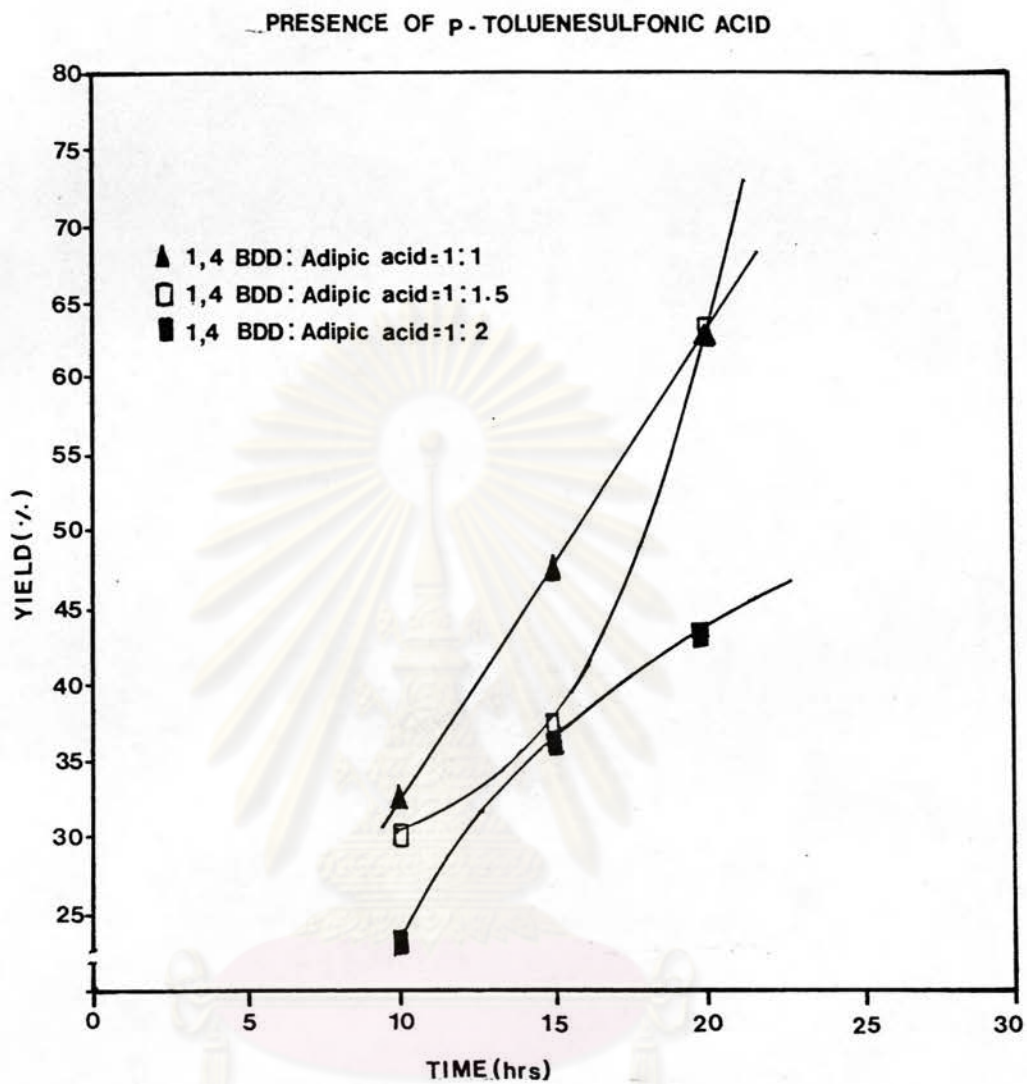


Fig.33. Graph of Poly(1,4-butylene-bis-(dibutyltin) adipate) prepared in p-toluenesulfonic acid

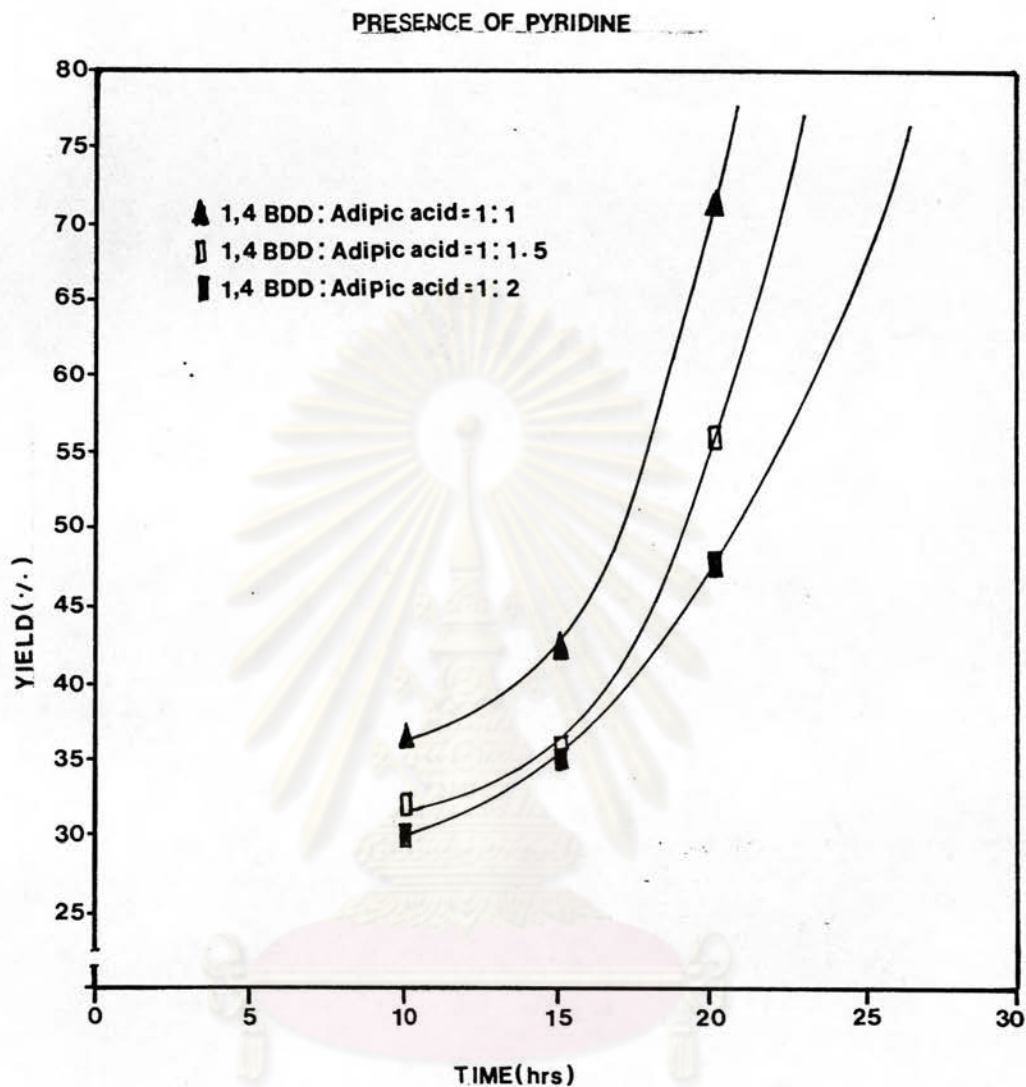


Fig.34. Graph of Poly(1,4-butylene-bis-(dibutyltin) adipate) prepared in pyridine

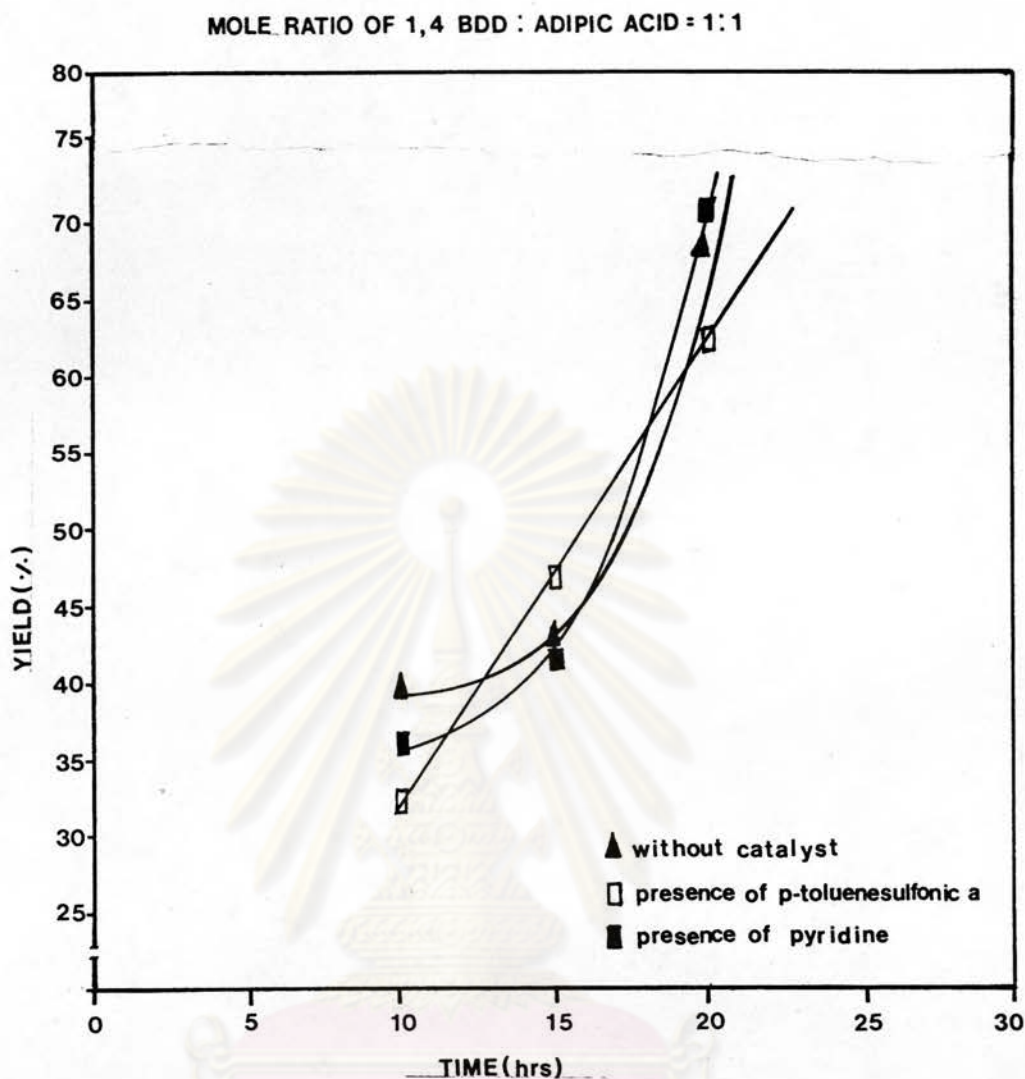


Fig.35. Graph of Poly(1,4-butylene-bis-(dibutyltin) adipate) prepared in mole ratio of 1,4 BDD : Adipic acid = 1:1

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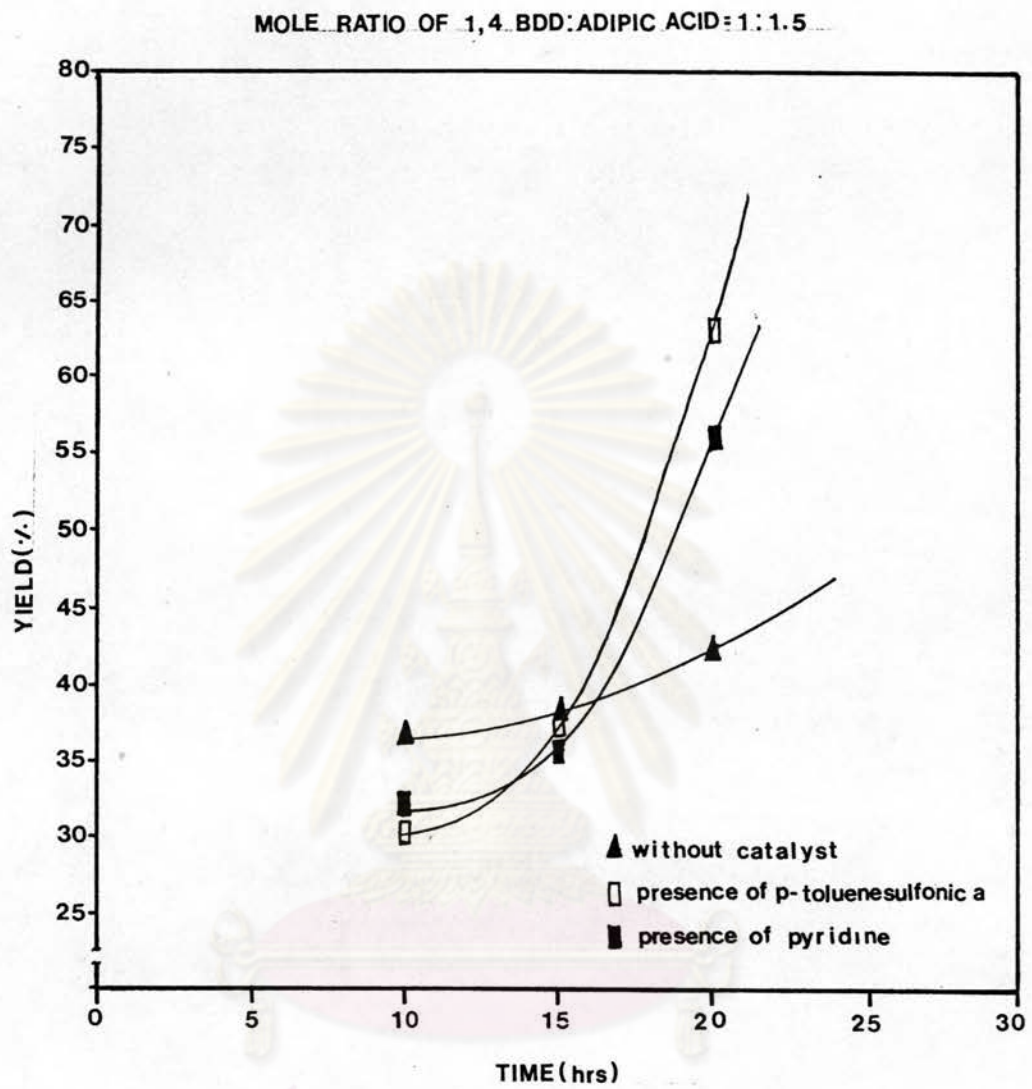


Fig.36. Graph of Poly(1,4-butylene-bis-(dibutyltin) adipate) prepared in mole ratio of 1,4 BDD : Adipic acid = 1:1.5

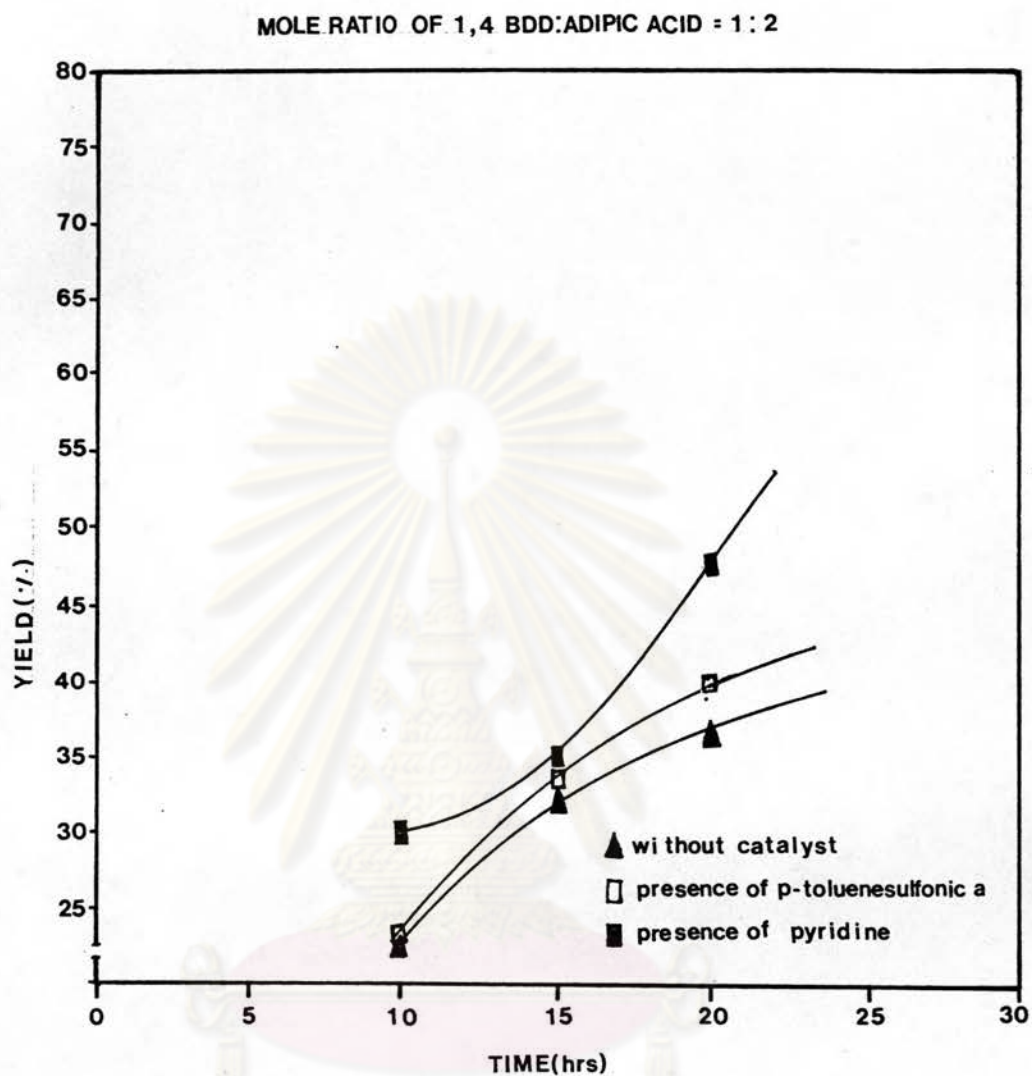


Fig.37. Graph of Poly(1,4-butylene-bis-(dibutyltin) adipate) prepared in mole ratio of 1,4 BDD : Adipic acid = 1:2

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Table 9. Show % conversion of 1,4-butylene-bis-(dibutyltin chloride) in Poly (1,4-BDDAA) in model system without catalyst

Time	Sample No.	Conc. of 1,4 BDD into poly((1,4 BDDAA) at time	Initial Conc of (1,4 BDD)	%Conversion
10	W10 1:10	0.4778	1.3807	34.60
	W10 1:1.5	0.4573	1.4554	31.42
	W10 1:2	0.2907	1.4465	20.01
15	W15 1:10	0.5778	1.5122	38.21
	W15 1:1.5	0.5088	1.5226	33.33
	W15 1:2	0.4342	1.4921	29.10
20	W20 1:10	0.8647	1.4465	59.78
	W20 1:1.5	0.4287	1.1313	37.89
	W20 1:2	0.4661	1.4604	31.92

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Table 10. Show % conversion of 1,4-butylene-bis-(dibutyltin chloride) in Poly (1,4-BDDAA) presence of p toluenesulfonic acid

Time	Sample No.	Conc. of 1,4 BDD into poly((1,4 BDDAA) at time	Initial Conc of (1,4 BDD)	%Conversion
10	C10 1:10	0.4101	1.4334	28.61
	C10 1:1.5	0.4035	1.4902	27.08
	C10 1:2	0.2794	1.3671	20.44
15	C15 1:10	0.6008	1.4338	41.90
	C15 1:1.5	0.5350	1.3900	33.65
	C15 1:2	0.5182	1.7612	29.43
20	C20 1:10	0.8142	1.4668	52.51
	C20 1:1.5	0.2093	1.4250	56.79
	C20 1:2	0.6799	1.7877	38.03

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Table 11. Show % conversion of 1,4-butylene-bis-(dibutyltin chloride)
in Poly (1,4-BDDAA) presence of pyridine

Time	Sample No.	Conc. of 1,4 BDD into poly((1,4 BDDAA) at time	Initial Conc of (1,4 BDD)	%Conversion
10	P10 1:10	0.5109	1.5549	32.86
	P10 1:1.5	0.4576	1.5781	29.00
	P10 1:2	0.4378	1.6181	27.06
15	P15 1:10	0.7081	1.8892	37.48
	P15 1:1.5	0.5622	1.7426	32.25
	P15 1:2	0.5563	1.7795	31.26
20	P20 1:10	1.0628	1.6756	63.43
	P20 1:1.5	0.9333	1.8525	50.38
	P20 1:2	0.7608	1.7576	43.29

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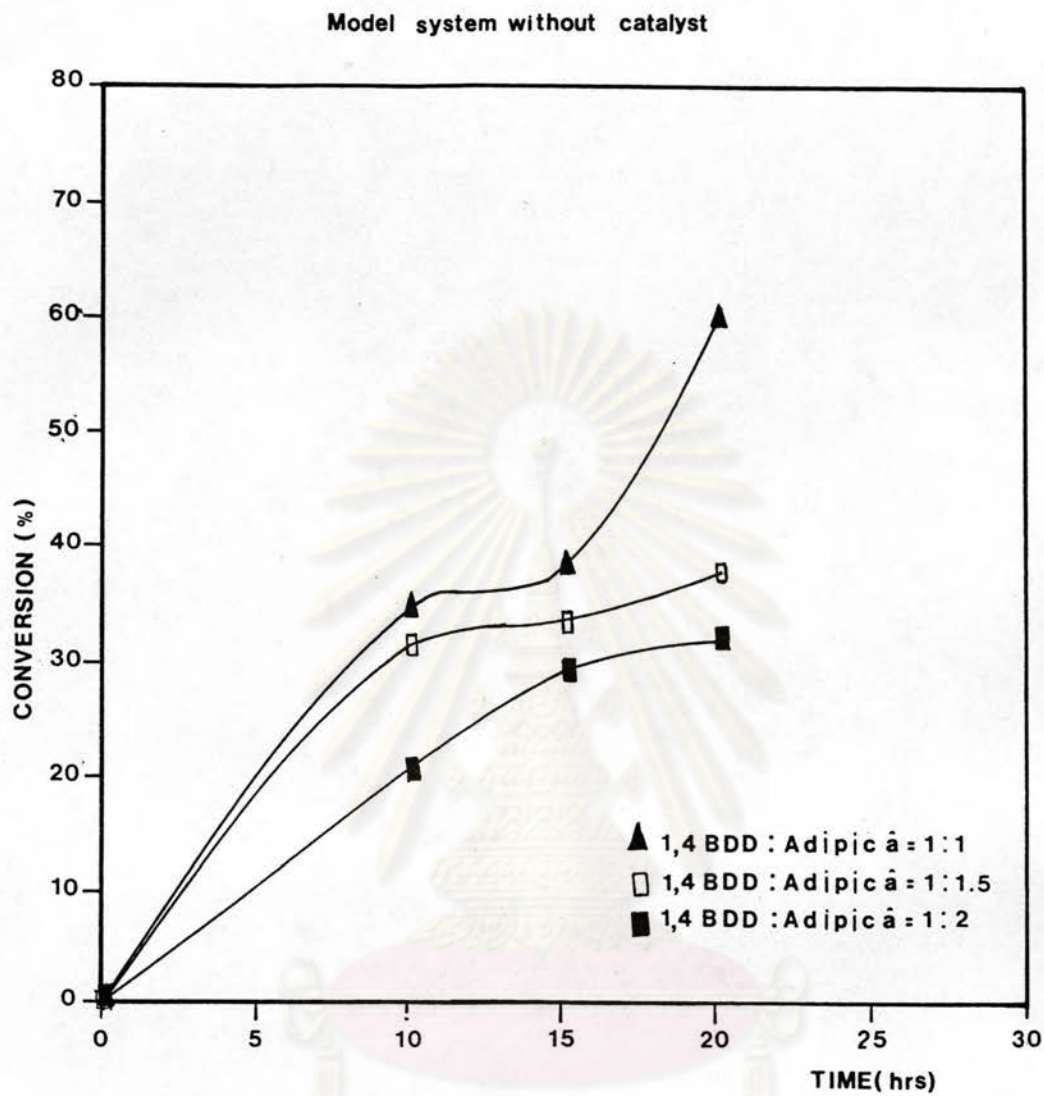


Fig.38. Show conversion of 1,4-butylene-bis-(dibutyltin chloride) in Poly(1,4-butylene-bis-(dibutyltin) adipate) prepared in without catalyst with time

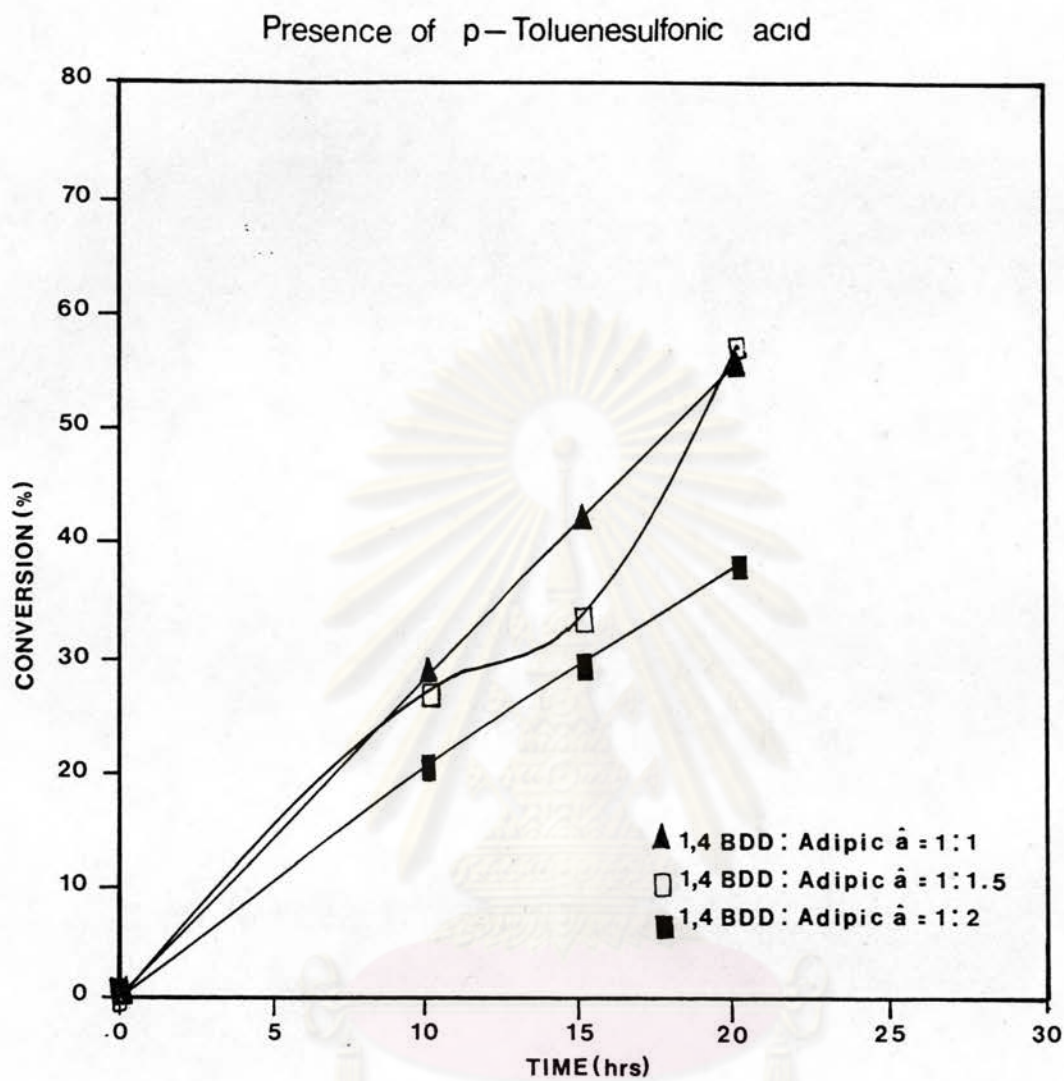


Fig.39. Show conversion of 1,4-butylene-bis-(dibutyltin chloride) in Poly(1,4-butylene-bis-(dibutyltin) adipate) prepared in p-toluenesulfonic acid with time

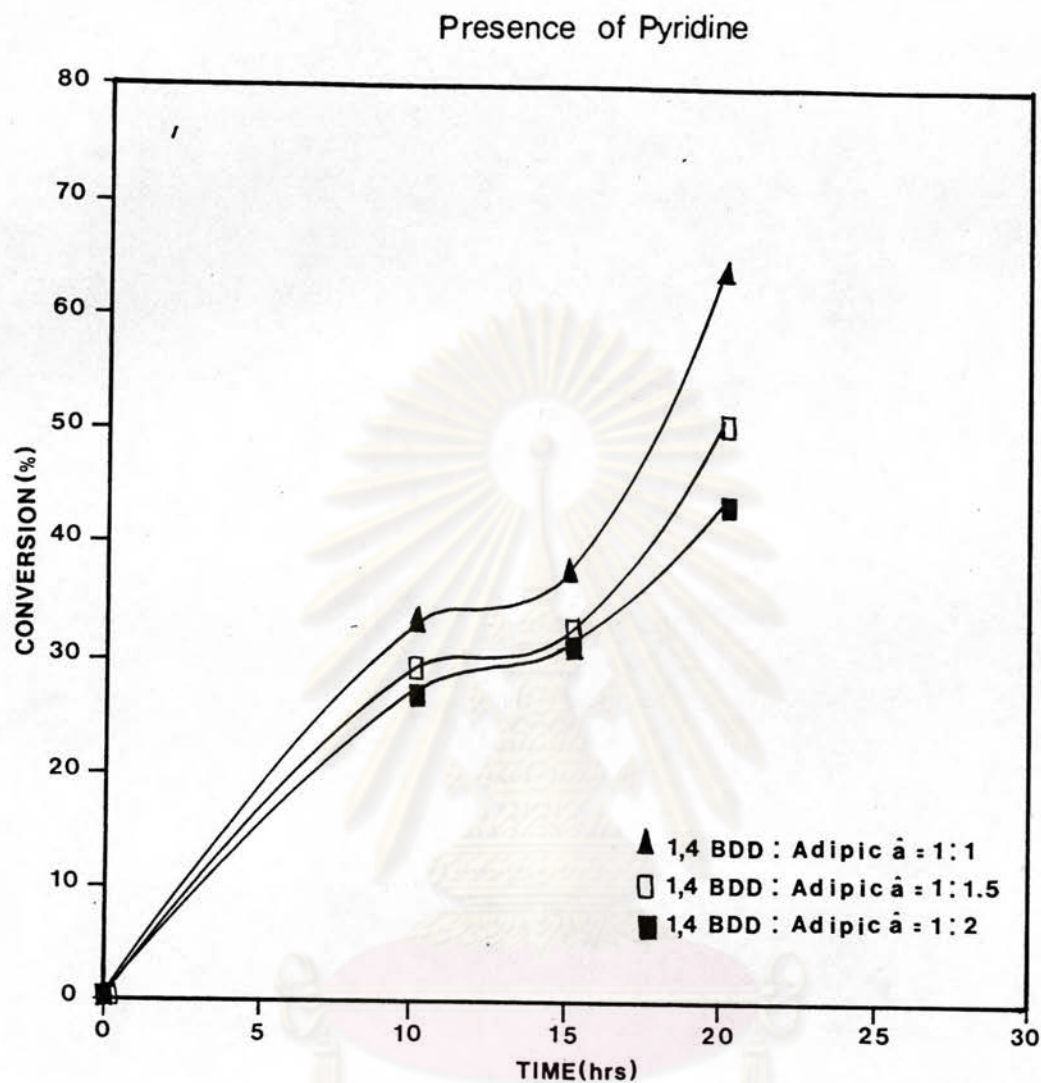


Fig.40. Show conversion of 1,4-butylene-bis-(dibutyltin chloride) in Poly(1,4-butylene-bis-(dibutyltin) adipate) prepared in pyridine

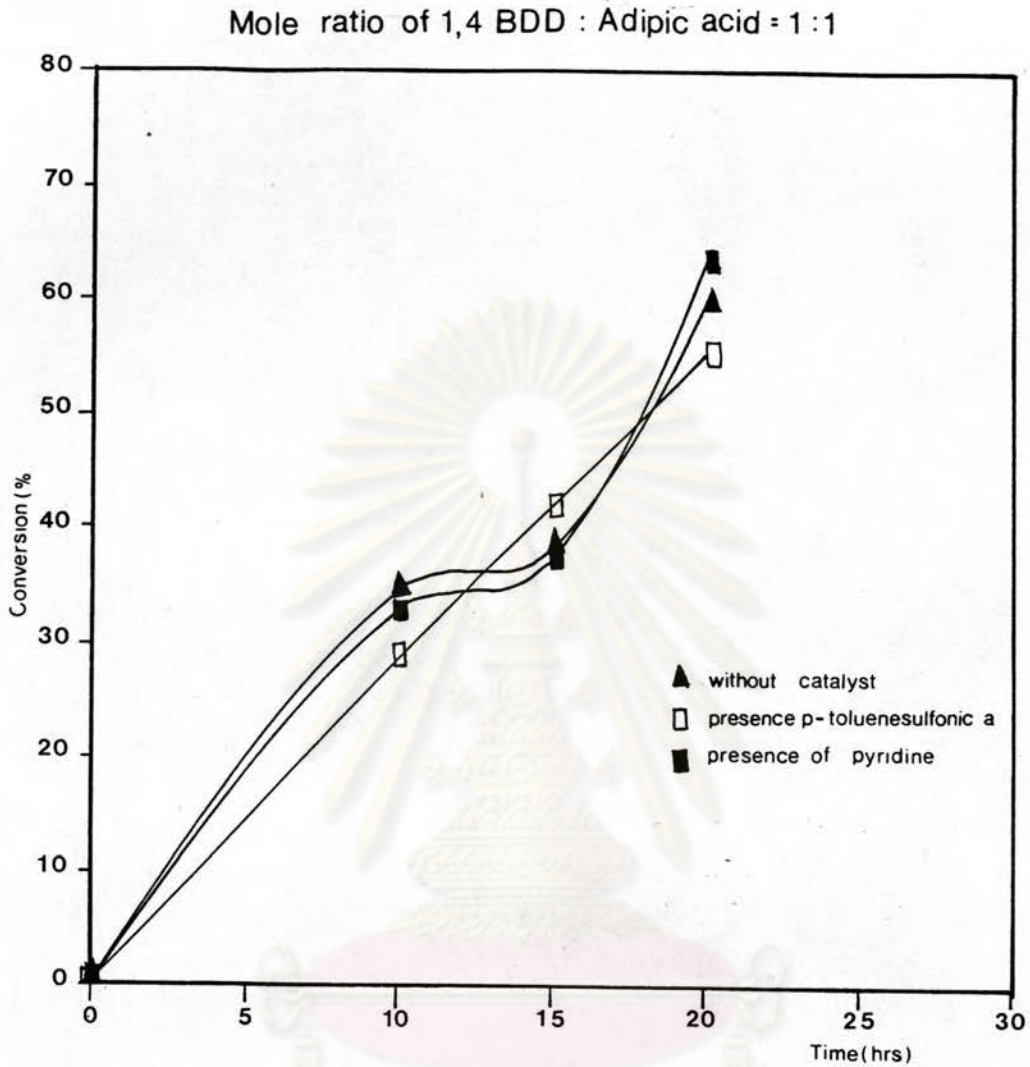


Fig.41. Show conversion of 1,4-butylene-bis-(dibutyltin chloride) in Poly(1,4-butylene-bis-(dibutyltin) adipate) prepared in mole ratio of 1,4 BDD : Adipic acid = 1:1

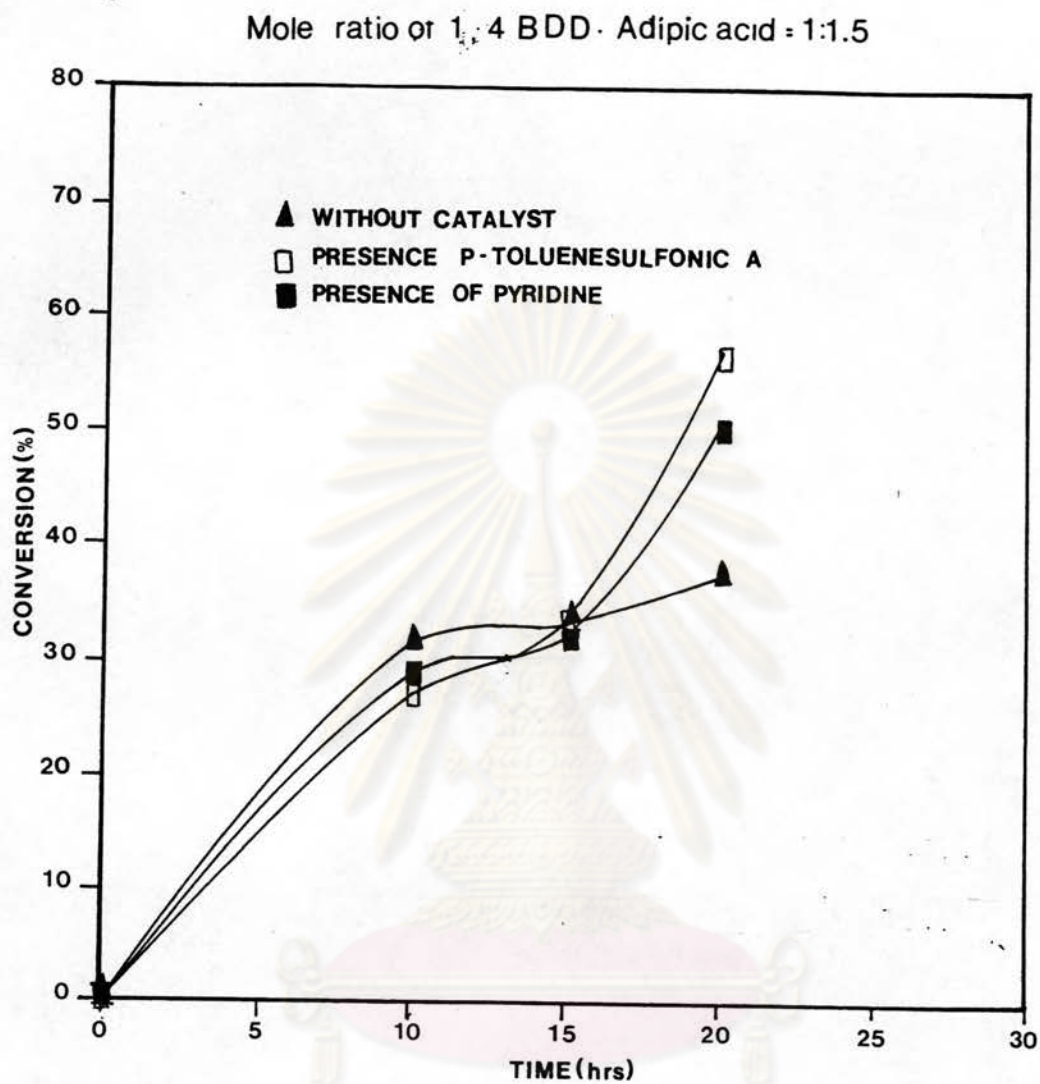


Fig.42. Show conversion of 1,4-butylene-bis-(dibutyltin chloride) in Poly(1,4-butylene-bis-(dibutyltin) adipate) prepared in mole ratio of 1,4 BDD : Adipic acid = 1:1.5

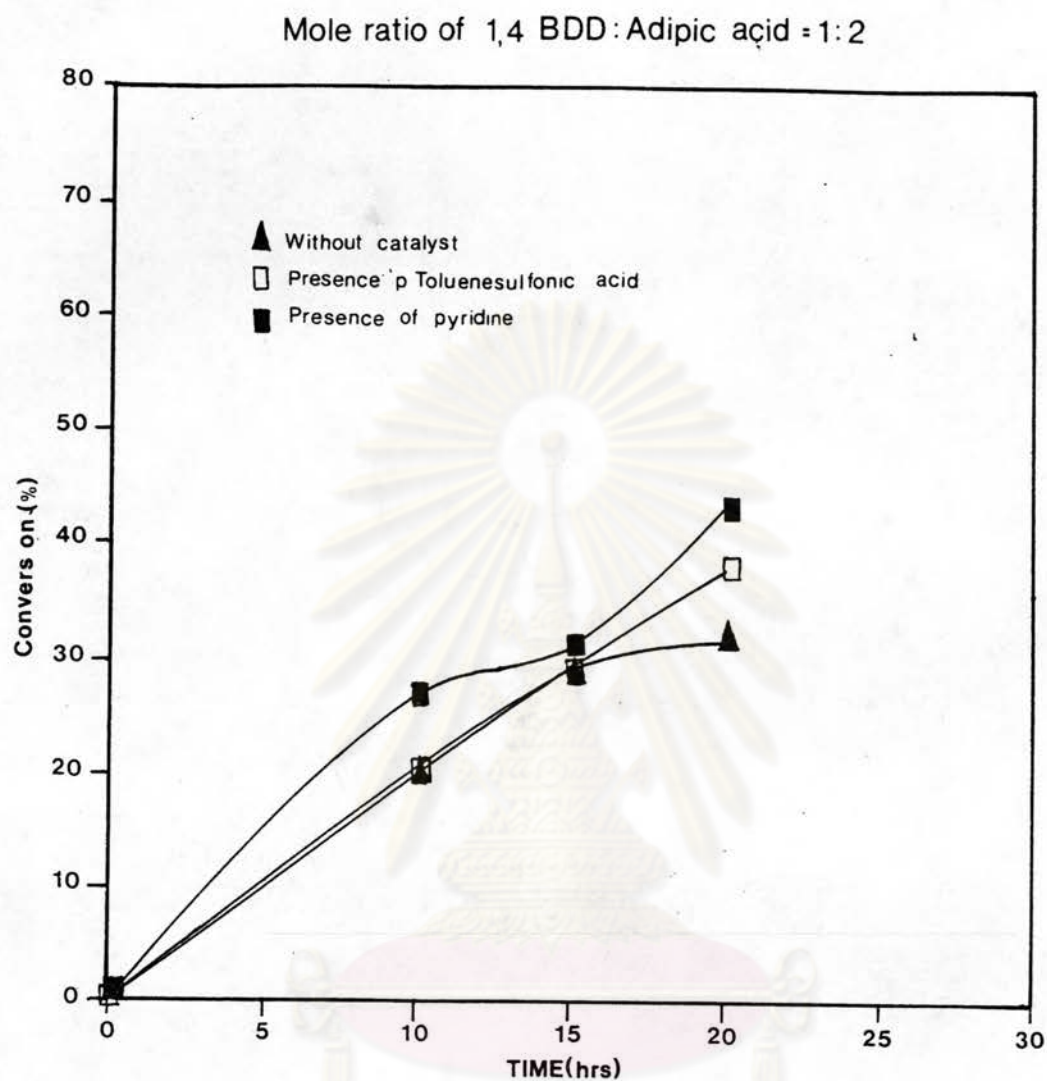


Fig.43. Show conversion of 1,4-butylene-bis-(dibutyltin chloride) in Poly(1,4-butylene-bis-(dibutyltin) adipate) prepared in mole ratio of 1,4 BDD : Adipic acid = 1:2

Table 12. Show Tg, Tc, Tm of

Poly(1,4-butylene-bis-(dibutyltin) adipate)

Time	Sample No.	Tg	Tc	Tm
10	W10 1:1.5	92	290	301
	W10 1:2	92	290	301
15	W15 1:2	93	284	298
	C15 1:1.5	93	284	293
	W15 1:1.5	93	292	300
20	P20 1:1.5	94	288	298
	W20 1:2	94	288	300
	P20 1:2	94	293	295

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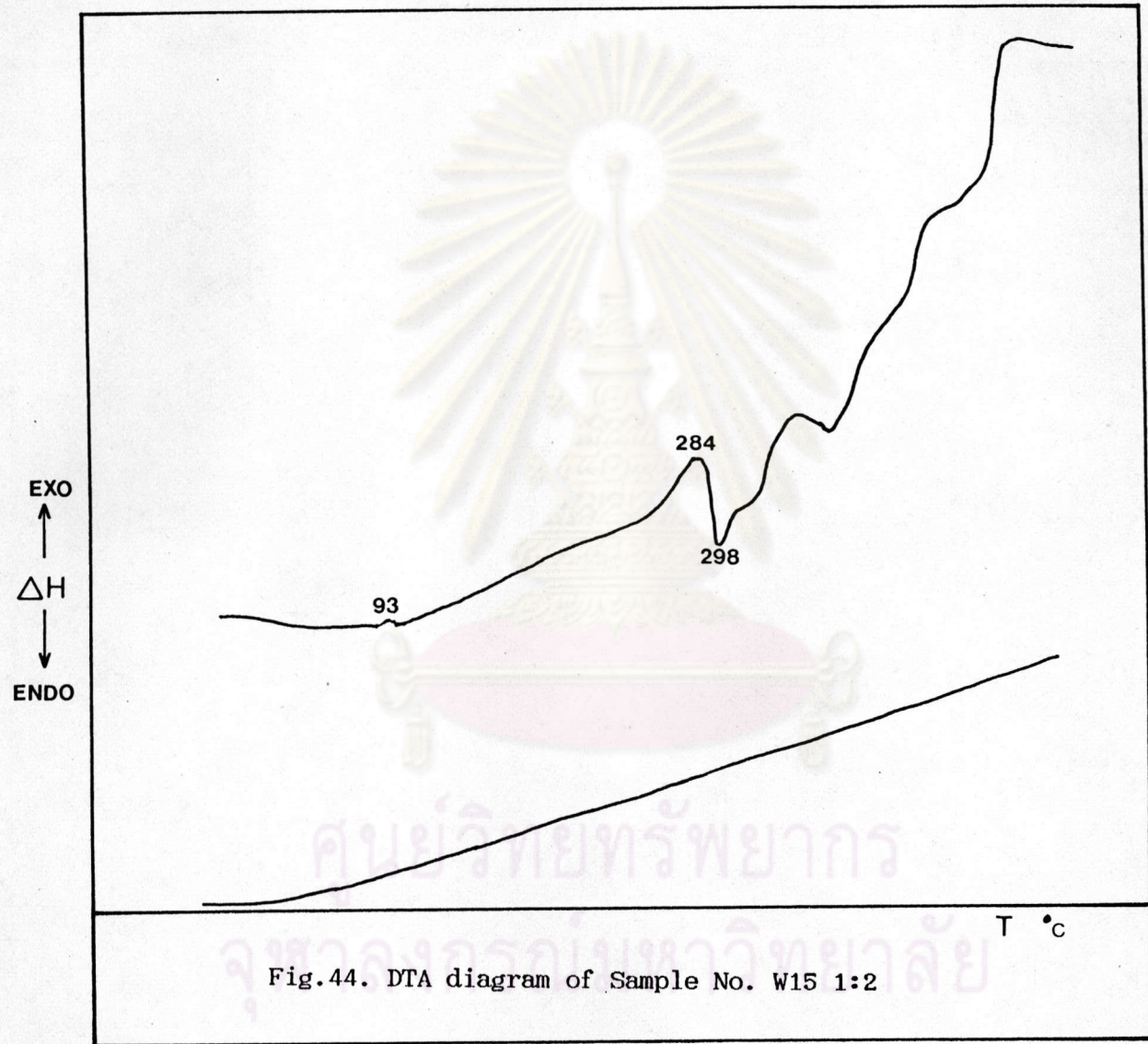


Fig.44. DTA diagram of Sample No. W15 1:2

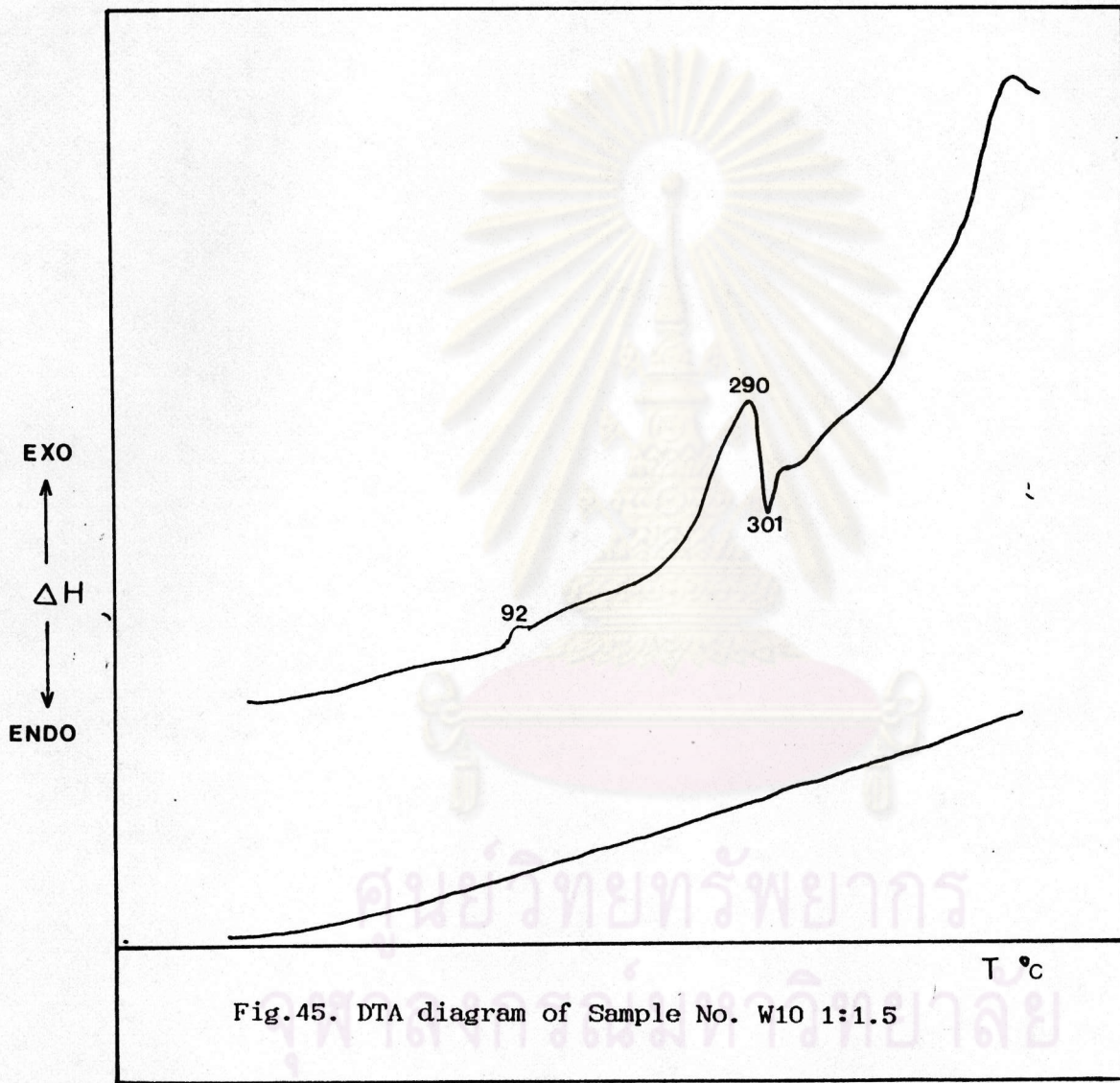
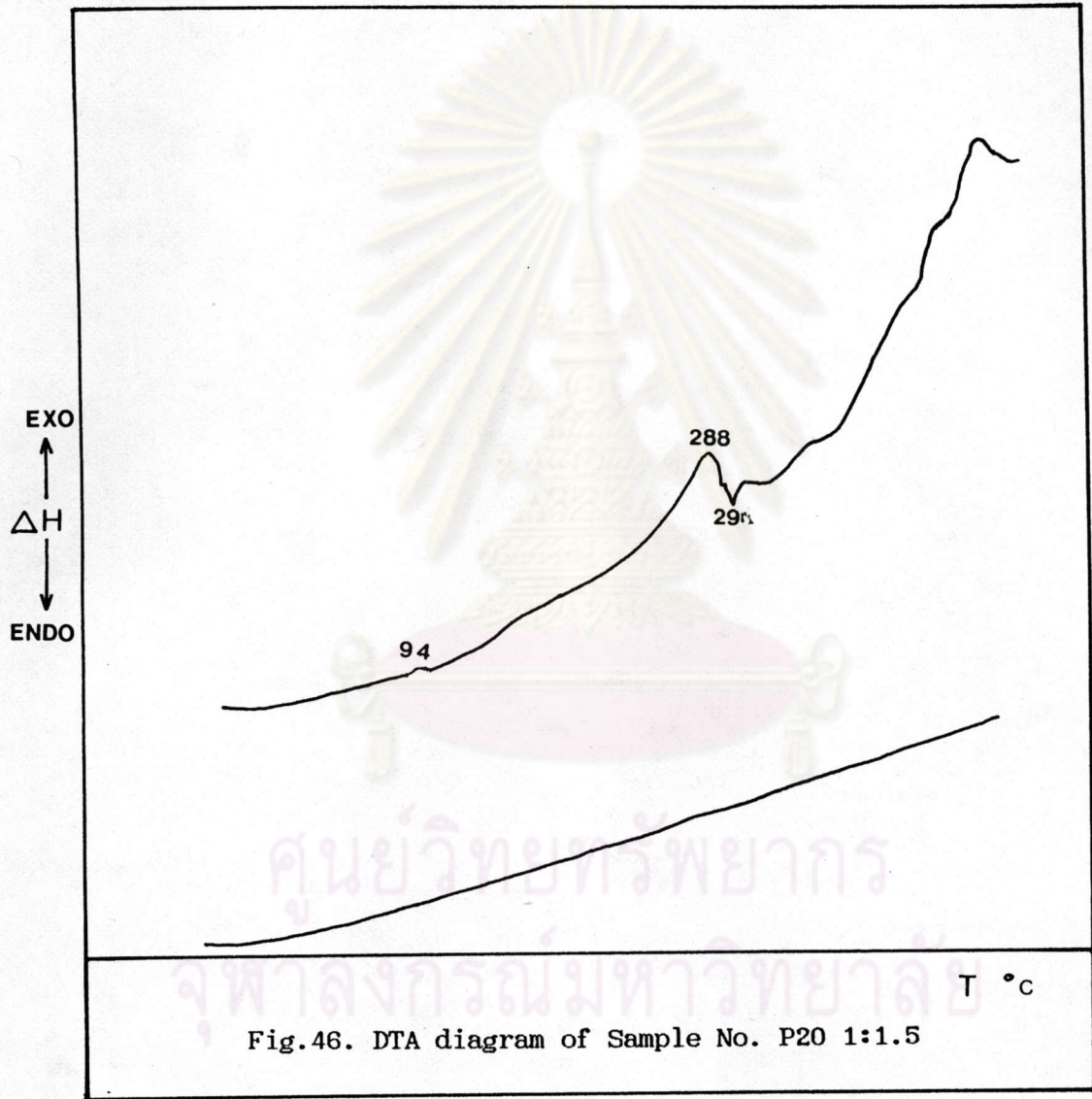


Fig.45. DTA diagram of Sample No. W10 1:1.5



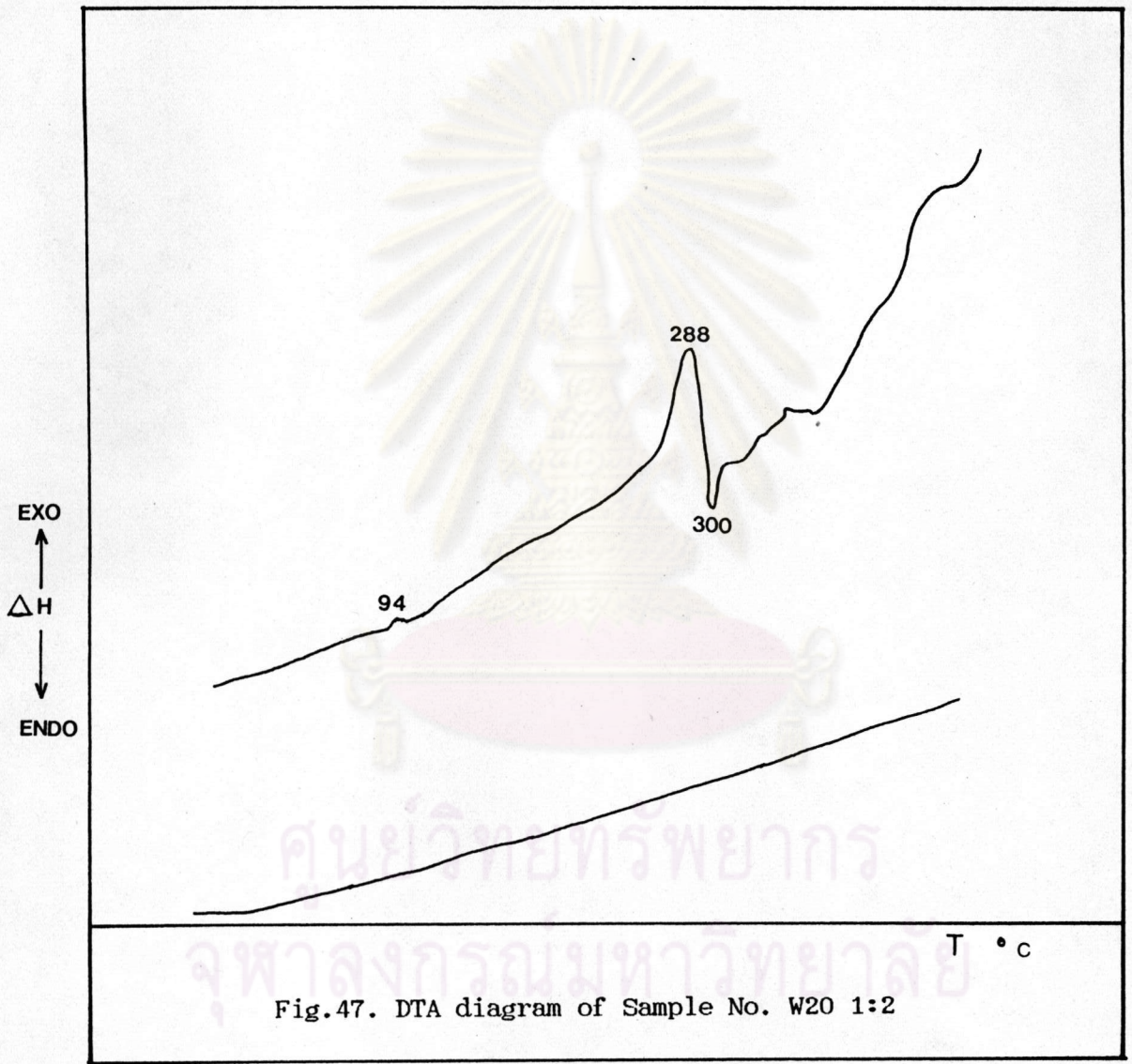
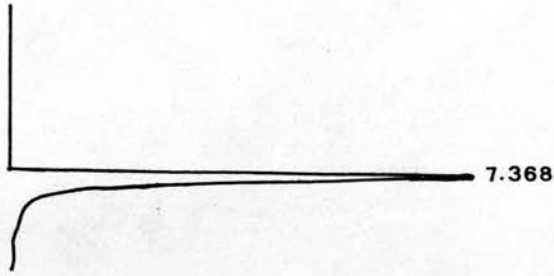


Fig.47. DTA diagram of Sample No. W20 1:2



Gas Chromatogram of THF



Gas Chromatogram of Benzene

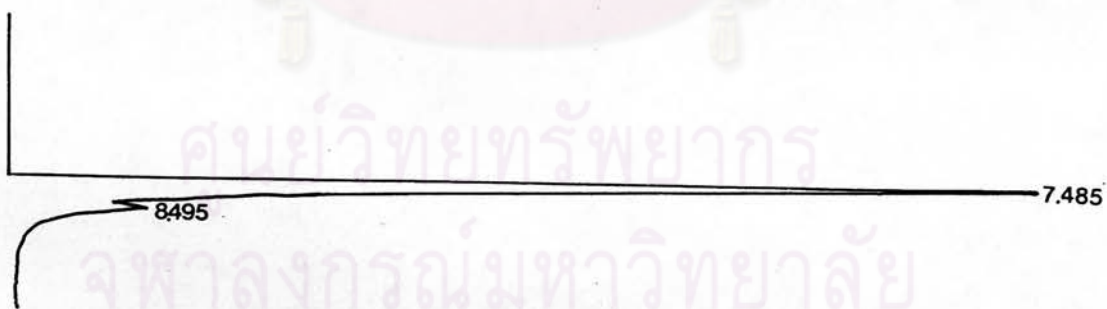


Gas Chromatogram of THF with Benzene

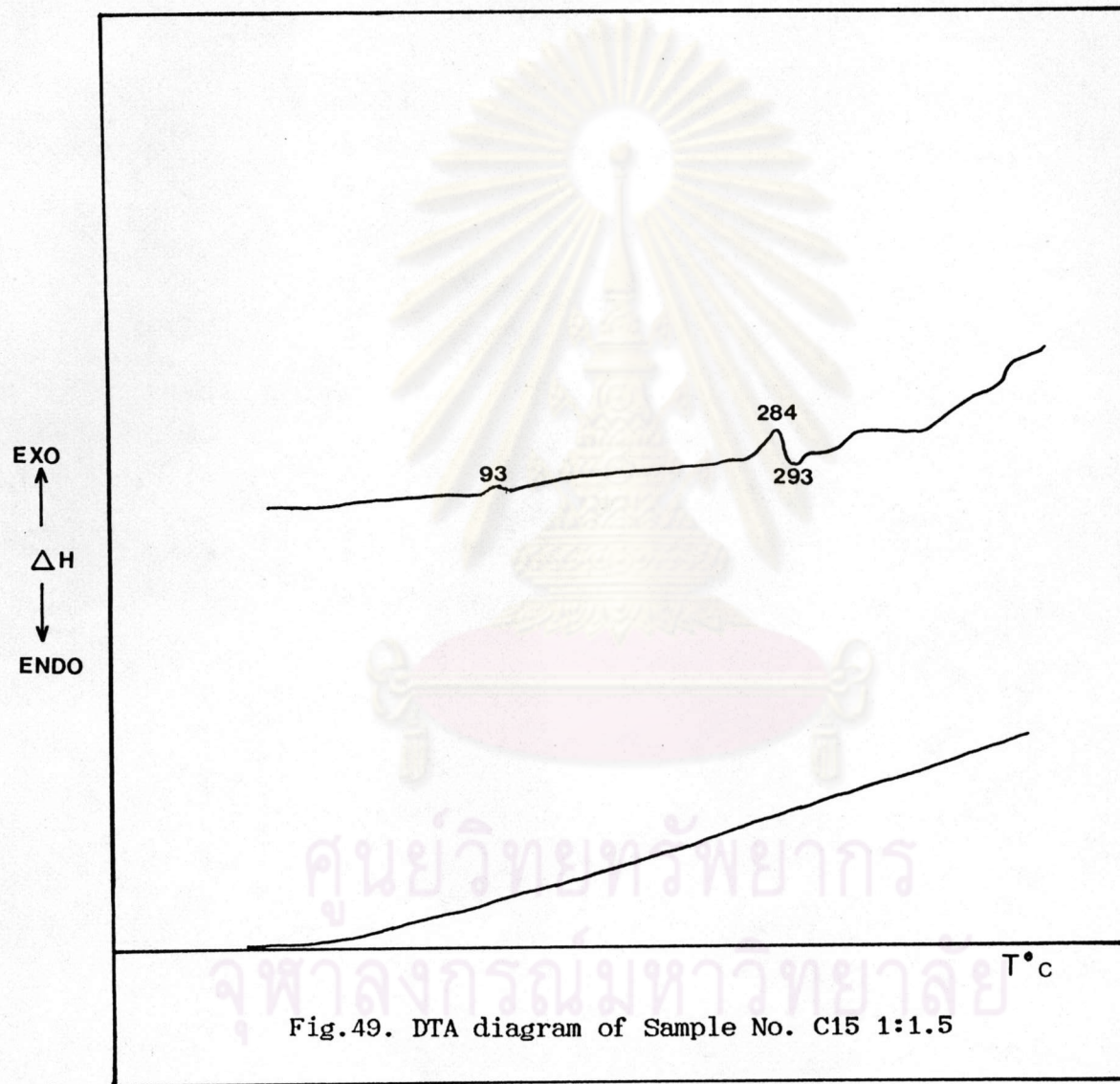
Fig.48. GC Chromatogram of Reaction Sec. 2.2.2



Gas Chromatogram of di-Grigard Reaction



Gas Chromatogram of di-Grigard Reaction



EXO
↑
ΔH
↓
ENDO

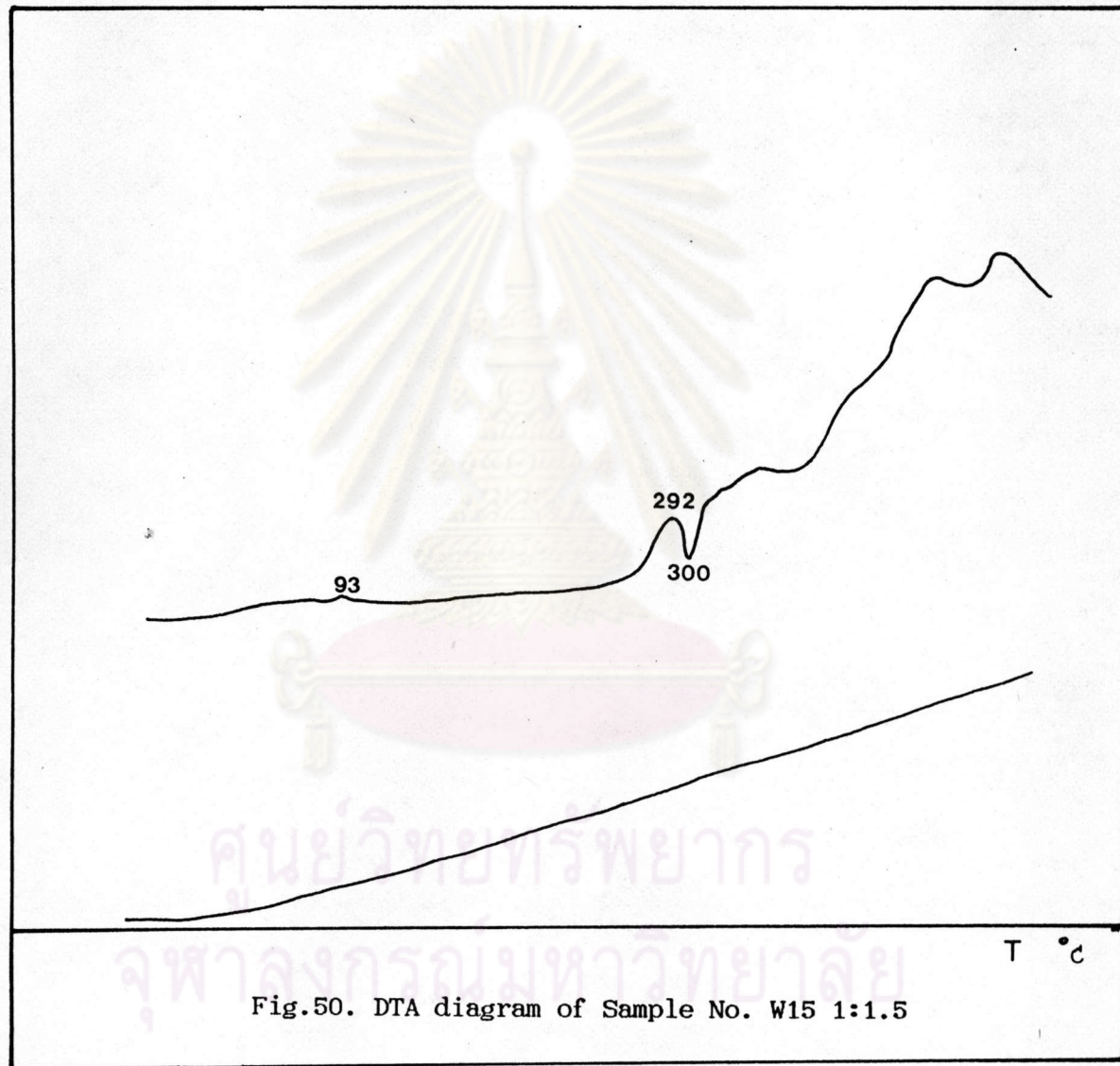
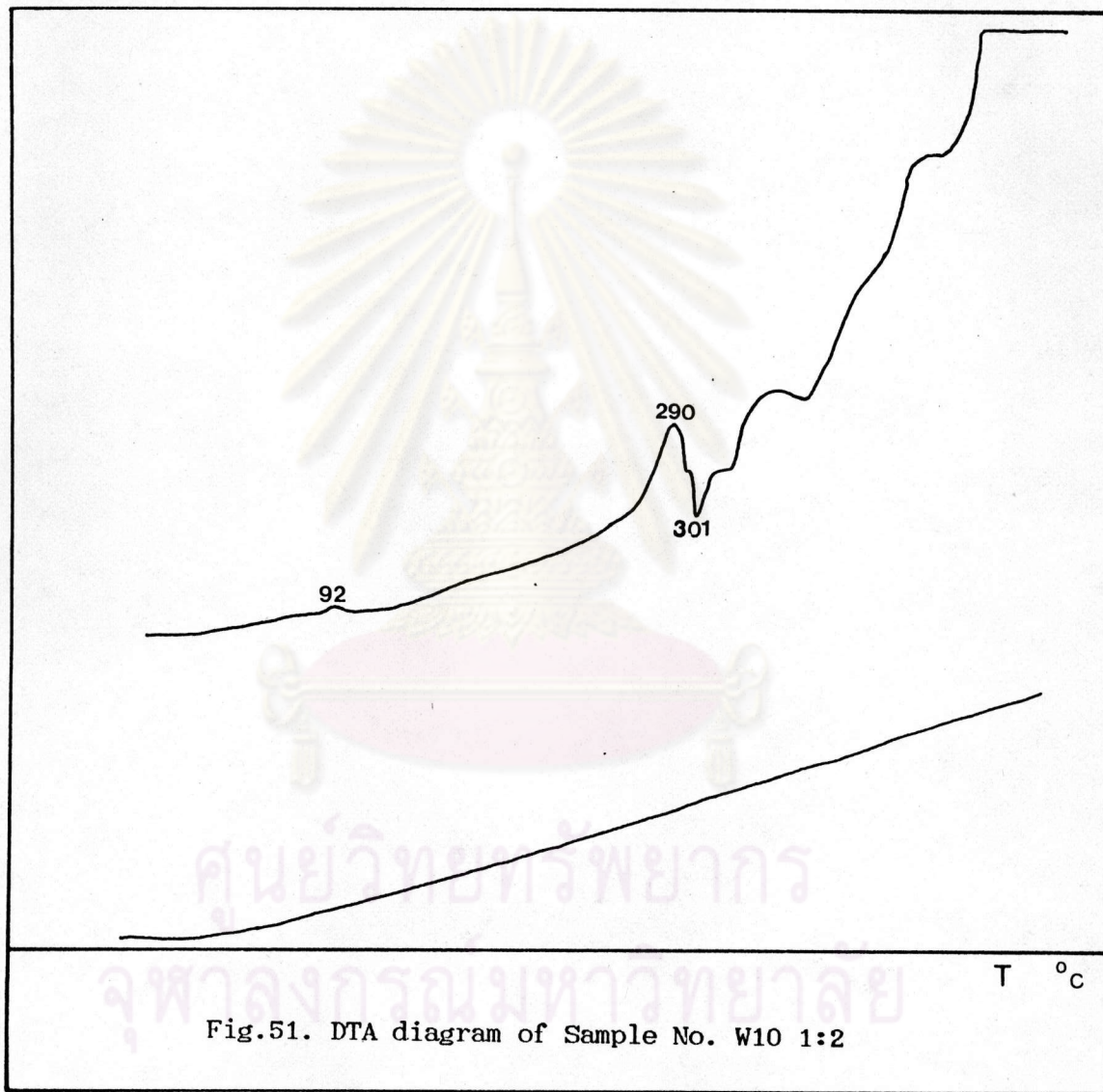


Fig.50. DTA diagram of Sample No. W15 1:1.5

EXO
↑
ΔH
↓
ENDO



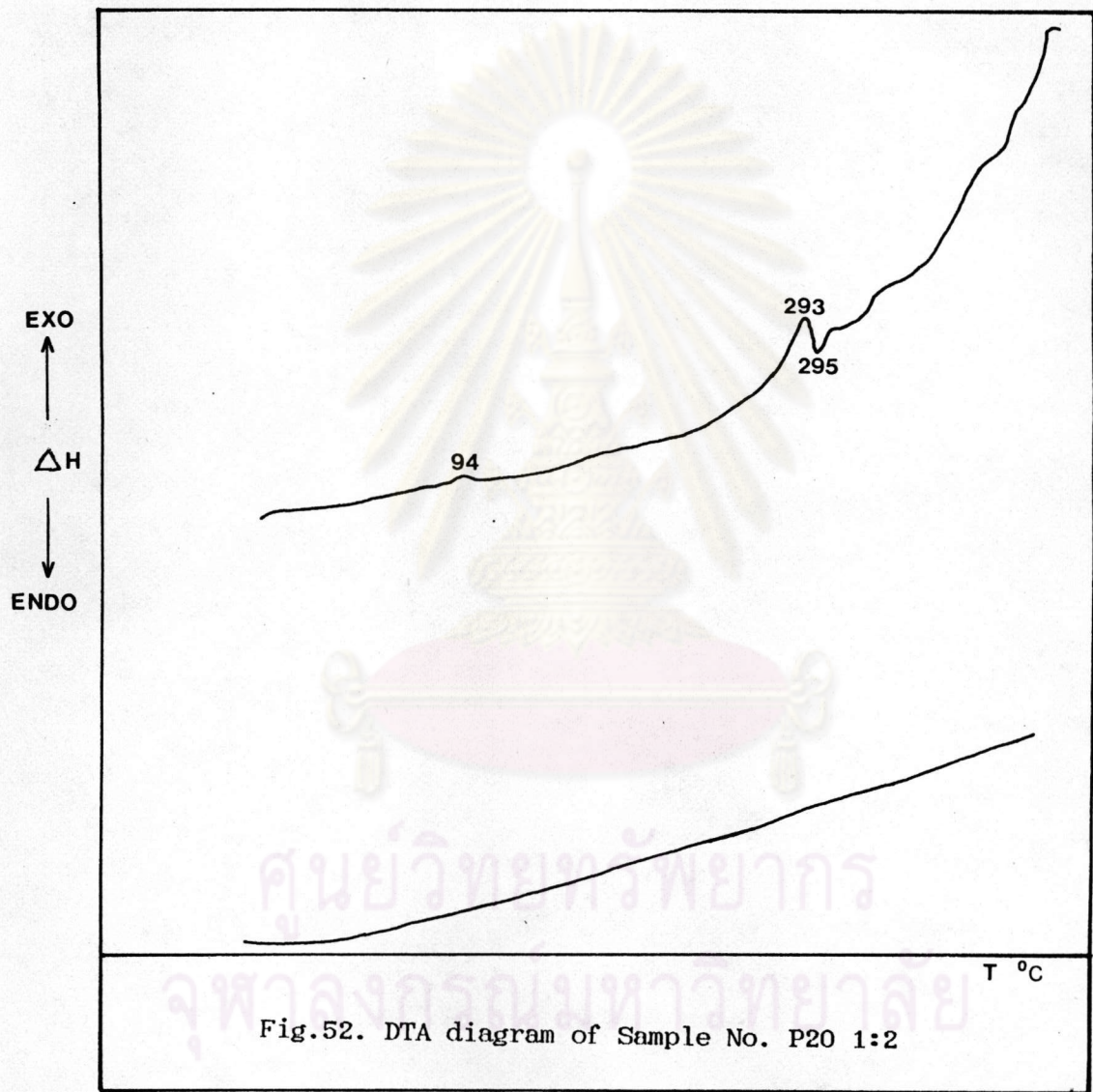


Fig.52. DTA diagram of Sample No. P20 1:2

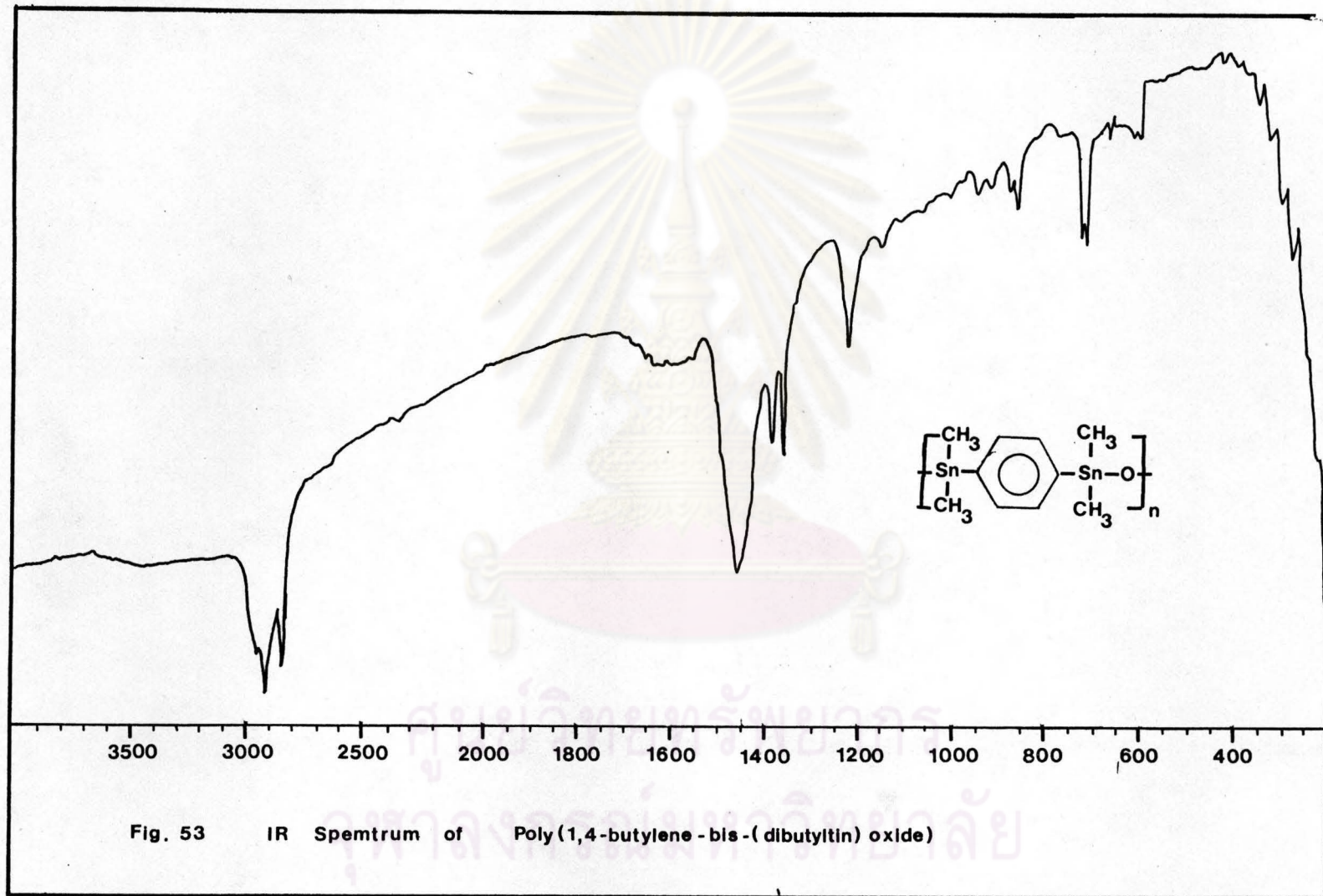


Table 13. Show Solubility of Poly(1,4-butylene-bis-(dibutyltin) adipate)

Polymer	Toluene	Benzene	Xylene	o'dichlorobezene	Chloroform	methylene
Poly(1,4 BDDAA)	x	x	x	/	x	x
Poly(1,4 BDDMA)	x	x	x	/	x	x
Poly(1,4 BDDO)	x	x	x	/	x	x
Poly(1,4 PDMO)	x	x	x	/	x	x

- * Poly(1,4 BDDAA) is Poly(1,4-butylene-bis-(dibutyltin) adipate)
 Poly(1,4 BDDMA) is Poly(1,4-butylene-bis-(dibutyltin) malonate)
 Poly(1,4 BDDO) is Poly(1,4-butylene-bis-(dibutyltin) oxide)
 Poly(1,4 PDMO) is Poly(1,4 phenylene bis-(dimethyltin) oxide)

x is insoluble

/ is soluble

ศูนย์วิทยทรัพยากร
 จุฬาลงกรณ์มหาวิทยาลัย