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Syntheses and characterization of novel nonlinear optical and electroresponsive polymers

Zou, Wan Kang, Ph.D.

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U·M·I
300 N. Zeeb Rd.
Ann Arbor, MI 48106

SYNTHESES AND CHARACTERIZATION OF NOVEL NONLINEAR OPTICAL AND ELECTRORESPONSIVE POLYMERS

by

WAN KANG ZOU

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ABSTRACT

SYNTHESES AND CHARACTERIZATION OF NOVEL NONLINEAR OPTICAL AND ELECTRORESPONSIVE POLYMERS

By

WAN KANG ZOU

Adviser: Professor Nan-Loh Yang

This thesis reports the synthesis and characterization of novel electroresponsive polymers for nonlinear optical investigations. Two kinds of conjugated polymer systems are considered: the π-electron conjugated system and the σ-electron conjugated system.

The first chapter introduces the general background of nonlinear optics and organic polymeric materials for nonlinear optical applications.

The second chapter describes the first synthesis and detailed characterization of a novel linear, high molecular weight and electroresponsive polymer - polystannane. The structure of this polymer was established using ^{119}Sn, ^{13}C and ^{1}H NMR. Its molecular weight, $\overline{Mn}$, was found to be ca. 1×10^4 based on ^{119}Sn NMR end group analysis and Vapor Pressure Osmometer. This polymer is highly photoactive, air sensitive, and its bleaching behaviors with photoscission are similar to polysilanes and polygermanes. The synthetic expertise developed in this area will allow us to explore a

broad spectrum of structural variations in this class of polymers. This is the first reported high molecular weight homonuclear tin-backbone polymer.

The third chapter is a description of the synthesis and characterization of σ-electron conjugated silicon-based polysilane polymers and study of their nonlinear optical properties. Polysilanes with four different combinations substituents were synthesized. The value of the third order optical nonlinearity $\chi^{(3)}$ was measured to be on the order of $2.0 \pm 0.6 \times 10^{-12}$ esu from the poly(phenylmethylsilane) thin films using OKG experiment. The response time of the nonlinear optical process associated with the electronic mechanism is found to be faster than 3 ps.

The sign of $\chi^{(3)}$ of the poly(phenylmethylsilane) solution was determined to be negative at 532 nm and positive at 1064 nm from Z-scan measurements. The value of $\chi^{(3)}$ at 532 nm is -7.0×10^{-12} esu, while $\chi^{(3)}$ at 1064 nm is relatively small, $+5.0 \times 10^{-13}$ esu. The near infrared (1064 nm) third order optical nonlinearity $\chi^{(3)}_{1064\ nm}$ is about 1.3×10^{12} esu using DFWM technique. The effects on the nonlinear optical properties due to the different substituents of polysilanes has been also studied. No significant third order optical nonlinearity difference was observed with different substituents.

An new polysilane with a pyridyl functional group is also reported in this chapter.

The fourth chapter gives a description of the synthesis

and characterization of three π-electron conjugated polymers: poly(4-butoxycarbonylmethylurethane); poly-bis(p-toluenesulfonate); and a soluble ladder polymer. Poly-4BCMU in PMMA matrix films with high optical transparency were prepared. The resonant third order optical nonlinearity $\chi^{(3)}$ of poly-4BCMU in PMMA matrix film was found to be about 3 x 10^{-10} esu with a subpicosecond (~12 ps) response time. The non-resonant $\chi^{(3)}$ term was found to be $3x10^{-11}$esu (~10 times smaller than the resonant $\chi^{(3)}$) with a faster than 1 ps response time. The relaxation time of the transient degenerate four-wave mixing grating in poly-4BCMU PMMA matrix films has been found to be laser energy fluency dependent.

To my parents, Xi Li Shi and Xue Jun Zou

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I am indebted to Dr. Lina Yang of Institute for Ultrafast Spectroscopy and Lasers and Photonic Application Laboratory The City College of The City University of New York for measurements of the third order nonlinear properties of polymers.

I am indebted to my parents and family for their faith and continued support. Finally I would like to thank my wife, Qiao Qiao Dong, for her love and support through all these years of my graduate studies at City University of New York.

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Chapter I. General Introduction

1.1. Fundamentals of Nonlinear Optics

Nonlinear optics is emerging as a new frontier of science and technology of photonics which offers challenges for both fundamental and applied research.[1-6] Photonics is the analog of electronics in that it describes the technology in which photons instead of electrons are used to acquire, store, transmit, and process information. The advantages of photonics as compared to electronics are the gain in speed, bandwidth and interconnectivity. Photonic switching can take place with femtosecond speeds, thus providing a gain in speed that is many orders of magnitude over that of electronic processes. Working at optical frequencies provides a tremendous gain in the bandwidth of information processing. Examples of nonlinear optical phenomena that are potentially useful in this area are the ability to alter, through intensity manipulation of control-beams, the frequency or color of trasmited light and to alter its transmission characteristics through a medium. It is the potential for providing these functions in suitable materials and devices that motivates much of the current fundamental and exploratory research in the field of nonlinear optics.

The invention of laser pulses has opened the door to the field of nonlinear optics. The observation of nonlinear optical effects requires the application of intense light.

In an intense optical field $\mathbf{E(t)} = \mathbf{Re}\ \varepsilon e^{i\omega t}$,[7] the nonlinear optical response of the bulk medium is represented by a constitutive relation for the dielectric polarization **P(t)**, i.e. the unit volume dipole moment:

$$\mathbf{P(t)} = \chi^{(1)}\mathbf{:E(t)} + \chi^{(2)}\mathbf{:EE(t)} + \chi^{(3)}\mathbf{:EEE(t)} + ...$$

In this expression, $\chi^{(1)}$ is the linear susceptibility, $\chi^{(2)}$ is the second order and $\chi^{(3)}$ is the third order nonlinear susceptibility.

The macroscopic behavior of the bulk material originating from the polarization of molecules induced by optical field **E** can be expressed as

$$\mathbf{P(t)} = \alpha\mathbf{:E(t)} + \beta\mathbf{:EE(t)} + \gamma\mathbf{:EEE(t)} + ...$$

Where α, β, and γ are tensor quantities which are known as polarizability, hyperpolarizability and second hyperpolarizability, respectively.

The second order and third order macroscopic nonlinear optical susceptibilities $\chi^{(2)}$ and $\chi^{(3)}$ can be related to the corresponding microscopic susceptibilities, β and γ by orientational averaging of β and γ in a molecular assembly and correcting for local field effects.

The second order nonlinear optical process occurs only in noncentrosymmetric media composed of noncentrosymmetric molecules. In general, for second order processes, fundamental frequencies at ω_1 and ω_2 combine to create a

third frequency at ω_3 ($\omega_3=\omega_1\pm\omega_2$). In the case of having ω_1 and ω_2 the same, second harmonic generation ($\omega + \omega = 2\omega$), optical rectification ($\omega - \omega = 0$) and liner electro-optic effect ($\omega + 0 = \omega$) are examples involving $\chi^{(2)}$. The third order nonlinearity can be observed in any materials. It gives rise to third order harmonic generation ($\omega + \omega + \omega = 3\omega$), optical Kerr effect[8] ($\omega - + = $), degenerate four wave mixing[9] (phase conjugation) and nonlinear refractive index (intensity dependent), n,
where

$$n = n_0 + n_2 I, \qquad n_2 = 16\pi^2\chi^{(3)}/c\varepsilon_1$$

The nonlinear index n_2 contributes to effects such as self-focusing, self-trapping and optical bistability, etc.. The n_2 is related to nonlinear dielectric permittivity ε_2 since $\varepsilon_2 = 8\pi\chi^{(3)}$. The quantity of ε_2^{-1} in erg/cm^2 characterizes the intramolecular energy density of the order of $Nh\omega_{i0}$, where $h\omega_{i0}$ is the transition energy difference which the optical field has to use to enlarge the electronic orbits.[1] It is obvious that materials with many easily displaceable electrons, e.g. organic π-electron systems, are favored and will exhibit a large nonlinearity. Theoretical calculation of the third order susceptibility of polydiacetylene by Ducuing[10] in the framework of Penn's one dimensional model indicate a strong relationship between $\chi^{(3)}$ and the delocalization of the π-electron cloud:

$$\chi^{(3)} \propto D^6/(E_F d)^3$$

where D is a delocalization parameter, d is the interatomic spacing and E_F is the Fermi energy. Similar results were obtained by Agrawal, et al,[11] in a tight-binding approximation using the Denkin and Mednis approach for nonlinear susceptibilities.

A large number of organic and polymeric materials have been shown to exhibit large , ultrafast second and third order nonlinear optical susceptibilities.[12-14] The most investigated polymer system is polydiacetylene (PDA), Which can exhibit third order susceptibilities as high as 8 X 10^{-10} esu for single crystals.[14] However, amorphous PDA exhibits a much smaller $\chi^{(3)}$. If practical applications of polymers in the fabrication of nonlinear optical devices is to be pursued, then new polymer materials with much higher nonlinear optical susceptibilities, higher laser damage thresholds, improved optical transparency, and improved processability must be developed.

1.2. Attributes and Requirements of Polymers for Nonlinear Optics

Organic and polymer structures exhibit unusually large, ultrafast second and third order nonlinear optical properties that are important to the fields of nonlinear optics and optical device technologies. These important properties have been demonstrated in a large number of structures, phases and states that include, as previously

reviewed,[13,15-20] organic crystals and films. Conjugated polymers, monomolecular films, liquid crystals, liquid crystal polymers, and high performance ordered polymers.[21,22] Polymers are the subject of intense research also because of additional advantages, such as synthetic and processing options that are not available with the single crystal and multiple quantum wells (MQW) classes of nonlinear materials. Structurally, polymers can be made as thin or thick films, bulk crystals, or liquid and solid solutions, and can be formed into layered film structures with molecular engineering providing different optical properties from layer to layer. Mechanically, the materials can be strong and resistant to radiation, shock, and heat. Another important attribute of polymers is that they show all the nonlinear optical properties, while MQW show third order but no optical amplification. There is no diffusion problems in polymers. Additionally, organic and polymeric materials can exhibit high laser damage thresholds, broad transparency ranges, and can be polished to high optical quality surfaces.

Recently, considerable interest has been directed to conjugated polymers. Theoretical estimations and experimental investigations have firmly established that larger electron delocalization is a prerequisite for large values of the nonlinear optical coefficients. Current theoretical and experimental interests have focused on large, ultrafast second and third order nonlinear optical properties observed for conjugated organic and polymer

systems.[23-27]

The focus of this thesis is on third order nonlinear optical polymers. The objective of this thesis work is to synthesize and characterize novel and existing classes conjugated polymers for nonlinear optical investigations. Two kinds of conjugated polymer systems, the π-electron conjugated system and the σ-electron conjugated system, are considered.

Chapter II. Synthesis and Characterization of High Molecular Weight Linear Polydibutylstannane

2.1. Introduction

The first linear high molecular weight soluble organotin homopolymer $(n\text{-}Bu_2Sn)_n$ was synthesized in this investigation by the Wurtz coupling of dibutyltin dichloride $(n\text{-}Bu_2SnCl_2)$ in a mixed solvent of toluene/heptane with small amounts of added crown ether. This polymer is highly absorbing at 371 nm in THF, approximately 38 nm, and 57 nm red shifted from the corresponding high molecular weight polygermanes[1] and polysilanes[2] respectively. Its photoactive, air sensitive, and bleaching behaviors accompanied by photoscission are similar to those exhibited by polysilanes and polygermanes. The polystannane differs significantly from the above polymers in its much higher light sensitivity. This polymer is thermally stable up to 220 °c, and soluble in common solvents such as chloroform, toluene, and THF.

High molecular weight polystannanes have never been reported in reference to its the synthesis and properties. Although the first oligomers with linear tin atom backbone $H[(C_2H_5)_2Sn]_nH$ ($n \leq 9$) were synthesized in 1964 by W. P. Neuman and J. Pedain,[3] interest in linear polystannanes was lacking until today due to the intractable nature of the derivatives synthesized earlier. Much of the scientific interest in catenated tin compounds has centered around

cyclostannanes $(R_2Sn)_n$ with three-, four-, five-, six-, seven-, and nine-membered rings,[4-8] and linear oligomer stannanes $R'-(R_2Sn)_n-R'$ with $n \leq 6$.[9-12] Our interest in this polymer was spurred by reported interesting properties of organosilane and organogermane high molecular weight polymers.

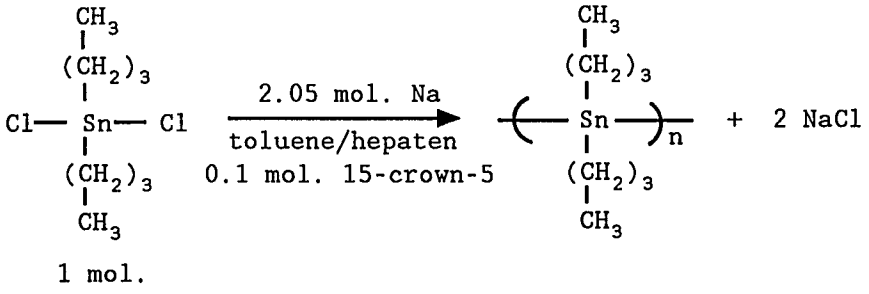
Silicon (Si), Germanium (Ge), and Tin (Sn) lie directly below carbon in the Periodic Table. The first soluble, high molecular weight polysilanes was developed in 1980.[13] These polymers chain is made up of only silicon atoms in the backbone, allowing significant delocalization of electrons along the polymer chain and giving these polymers highly unusual properties quite unlike carbon based polymers. An explosive rebirth of interest in polysilanes was stimulated and the subject continues to be at the cutting edge of material chemistry research activities today.[14-18] It is now clear that high molecular weight polysilane represent a new class of radiation sensitive polymers for which a number of applications have been reported. They have been used as radiation sensitive materials for microlithography, [18] lithography,[19,20] photoinitiators for vinyl polymerizations[21] and as ceramic precursors.[22] The first soluble, high molecular weight of polygermanes was developed in 1985.[23] It also exhibited optical properties similar to polysilanes.[24] It would be of fundamental interest to prepare organostannane (organotin) high molecular polymers for the purpose of establishing structure/property relationship for homonuclear chain

polymers based on Group IV A atoms.

2.2. Experimental

2.2.1. Polymerization of Dibutyltin Dichloride

Dibutyltin dichloride (97%) was purchased from Aldrich. It was carefully fractionally distilled immediately prior to use. Toluene and heptane were dried by refluxing over sodium metal for 48 hours and distilled before use. The sodium used in the polymerization was purchased from Fluka as a 30 wt.% dispersion in toluene. Operations were conducted using syringe techniques or in the nitrogen atmosphere of a dry box. The entire apparatus was assembled and flamed to remove residual moisture from the system. All reactions were carried out under dry nitrogen atmosphere. The synthetic reaction can be depicted as follows:



Into a dry 500 ml three-necked round bottom flask equipped with a condenser, argon inlet, and addition funnel was placed toluene (144.5 ml), heptane (25.5 ml), 15-crown-5 (3.02 g, 0.0137 mol.), and sodium dispersions (10.50 g,

0.137 mol, 30 wt% in toluene). A solution of toluene (30 ml) containing 20.32 g (0.067 mol.) of distilled dibutyltin dichloride was added to the addition funnel, and the flask was heated to 60 °C in an oil bath. The solution of dibutyltin dichloride in toluene was added dropwise under protection against ambient light to the well-stirred mixture in the flask. After the completion of the addition (approximates 30 min.), the reaction was stirred at 60 °C for 14 hours. The mixture was cooled to room temperature and transferred to a double ended sintered glass filter tube to remove salts (NaCl) formed and traces of unreacted sodium by filtration under dry nitrogen atmosphere. Most of the toluene and heptane were then stripped off at 50 °C under vacuum to give a concentrated solution. The polymer was obtained by precipitation of the residual reaction mixture from oxygen free anhydrous methanol ten times of its volume. The precipitate was dried under vacuum (2 mm Hg) at 55 °C for 8 hrs to yield 6.31g (40.5 %) of a somewhat tacky yellow solid. It is soluble in toluene, chloroform, and tetrahydrofuran at room temperature.

2.2.2. Elemental Analysis of Polydibutylstannane

Polymer samples were sealed in glass tube in a dry box for Elemental analysis performed by Galbraith Laboratories, Inc. (P.O. Box 51610, Knoxville, Tenn 37921).

2.2.3. NMR Characterization of Polydibutylstannane

All NMR spectra were obtained with a IBM WP-200 SY

Fourier Transform NMR Spectrometer operated at 200 MHz for proton using Bruker softwares. The chemical shifts were referenced to tetramethylsilane at 0 ppm for ^{1}H spectra, to $CDCl_3$ at 77 ppm for ^{13}C spectra, and to tetramethyltin at 0 ppm for ^{119}Sn spectra. Spectral quantitative evaluation were obtained under conditions all atoms of concern were completely relaxed. Distortionless Enhanced Polarization Transfer (DEPT) ^{13}C NMR experiment was performed to identify the CH_3 and CH_2 groups using a DEPT program from Bruker software. All tin spectra were obtained in a 10 mm multi nuclei probe.

2.2.4. Determination of Molecular Weight of Polydibutylstannane

The molecular weight of polydibutylstannane was estimated from ^{119}Sn NMR end group analysis and Vapor Pressure Osmometer (VPO). measurements were carried out on an UIC 070 VPO Semi-automatic Vapor Pressure Osmometer at 45 °C with benzil as calibration standards and toluene as solvent. VPO was placed in an plastic tent purged with dry nitrogen and measurements were conducted under the dry nitrogen atmosphere.

2.2.5. Thermal Stability of Polydibutylstannane

The thermal stability of polydibutylstannane was determined by TGA technique with a DuPont Thermal Analyzer, Model 990. The sample size of polymer was 18 mg. The heating rate was 10 °C/min. from 50 °C to 350 °C under a

100 ml/min. flow of nitrogen.

2.2.6. UV Spectroscopy and Photophysics of Polydibutylstannane

The UV spectra were obtained on a Varian DMS 300 UV Visible Spectrophotometer. Radiation source used was a high pressure mercury lamp. No quantitative photometry was performed. However, all irradiations experiment, e.g. for polysilane and polystannane, were conducted under equivalent radiation intensity

2.3. Results and Discussion

2.3.1. Elemental Analysis

The values for polymer compositions obtained by elemental analysis are consistent with the theoretical values for the expected polystannane structure:

Table 2-1. Results of elemental analysis

Elements		Carbon (C)	Hydrogen (H)	Tin (Sn)
Theoretical Value (%)		41.28	7.73	50.99
Exp. Value (%)	Sample #10*	42.10	7.68	50.41
	Sample #11**	42.62	8.09	50.42

* Polydibutylstannane obtained under reaction conditions stated in the Table 2-2, exp. #10.

** Polydibutylstannane obtained under reaction conditions stated in the Table 2-2, exp. # 11.

2.3.2. Determination of Structure by ^{1}H, ^{13}C, and ^{119}Sn NMR Spectra

Figure 2-1 shows a ^{1}H NMR spectrum of polydibutylstannane in $CDCl_3$ at room Temperature. A triplet at 0.90 ppm is due to the methyl protons of the butyl group; a second triplet at 1.2 ppm, due to methylene protons next to the Sn atom. The multiplet at 1.34 ppm is assigned to methylene protons next to the methyl group; the multiplet at 1.53 ppm, due to methylene protons connected to carbon two bonds away from the Sn atom. The ratio of integrated absorptions of protons in $(CH_2)_3/CH_3$ matches the required value of 2/1. Figure 2-2 shows a ^{1}H NMR spectrum of dibutyltin dichloride monomer. A triplet at 0.93 ppm is due to the protons of methyl group. The multiplet at 1.44 ppm

is assigned to methylene protons next to the Sn atom. The absorptions in the region 1.65 ppm to 2.15 ppm are assigned to the protons of the two remaining methylene groups.

Figure 2-3 shows a DEPT NMR spectrum of this polymer. The peak with positive intensity at 13.67 ppm is due to the C_1 in CH_3 group. The inverted peak at 10.35 ppm, is assigned to the methylene carbon (C_4) next to the Sn atom. The absorptions at 27.75 ppm and 32.95 ppm are assigned to carbons C_3 and C_2 of the two remaining methylene groups respectively. In comparison with DEPT NMR spectrum of dibutyltin dichloride monomer (Figure 2-4), the absorption at 26.0 ppm due to Sn bonded C_4 was shifted significantly upfield to 10.35 ppm. This marked difference between monomer and polymer chemical shift is caused by the substitution of Cl atoms in monomer by Sn atoms in polymer. Since Cl is more electronegative than Sn, the substitution of Cl by Sn results in C_4 being more shielded. Hence, an upfield chemical shift from 26.00 ppm to 10.35 ppm was observed. The absorption of C_3 is upfield to C_2 because of its closer proximity to Sn compared to C_2.

Figures 2-5 and 2-6 show ^{13}C NMR spectra of polymer and monomer with their assignments respectively. In the polymer spectrum (Fig. 2-5), besides the four main peaks, weak singlets at 9.17 ppm, 12.75 , and 30.72 ppm are tentatively assigned to cyclic oligomers and end groups. Absorptions observed in ^{119}Sn NMR (Fig. 2-7) at -252.8 ppm and -100.5 ppm are assigned to cyclic and end groups respectively. In the ^{1}H NMR, no distinct absorptions due to

cyclic oligomers and end groups were observed, perhaps due to their overlap with main peaks.

Similar to polysilanes[25] and polygermanes,[23] the condensation polymerizations with a slight excess of sodium metal dispersion can lead to cyclic compounds and low molecular weight oligomers. They are always formed along with polymer during the synthesis. The amount of the oligomers formed depended on the synthetic conditions [26,27] (see Section 2.3.3).

Based on ^{119}Sn NMR literatures,[8-11,28-35] ^{119}Sn NMR chemical shifts (relative to $SnMe_4$ at 0 ppm) of tin compounds relevant to this work are shown as follows:

Tin Compound	Chemical Shift of Sn* (ppm)
R_3-Sn*-Sn	-80 ~ -110
R_2-Sn-Sn*-Sn	-220 ~ -290
R-Sn*(SnR_3')$_3$	-450 ~ -500

where R is alkyl group. The Sn resonances in trialkyltin (R_3Sn) occur at -80 ppm to -110 ppm; the Sn in dialkyltin (R_2Sn) resonances, at -220 ppm to -290 ppm; and the Sn in alkyltin (RSn) resonances, at -450 ppm to -500 ppm. For ^{119}Sn NMR spectrum of polydibutylstannane in $CDCl_3$ (Fig. 2-7), the absorption -268.0 ppm is assigned to the resonance of Sn in the polymer backbone (-$SnBu_2$-). The absorption at -252.8 ppm is assigned to the resonance of tin in cyclostannanes. The absorption at -100.5 ppm falls in the chemical shift range for tin atom connected to only one

other tin atom (-80 ppm to -110 ppm) and is therefore assigned as the end groups. Any tin atom directly bonded to more than one tin atom has its chemical shift upfield of -200 ppm due to more chemical shielding by tin. Figure 2-8 shows a ^{119}Sn NMR spectrum of dibutyltin dichloride monomer. The absorption of Sn in dibutyltin dichloride appears at 163 ppm, indicating more than 400 ppm chemical shift difference due to the two Cl atoms having been replaced by two Sn atoms after the polymerization.

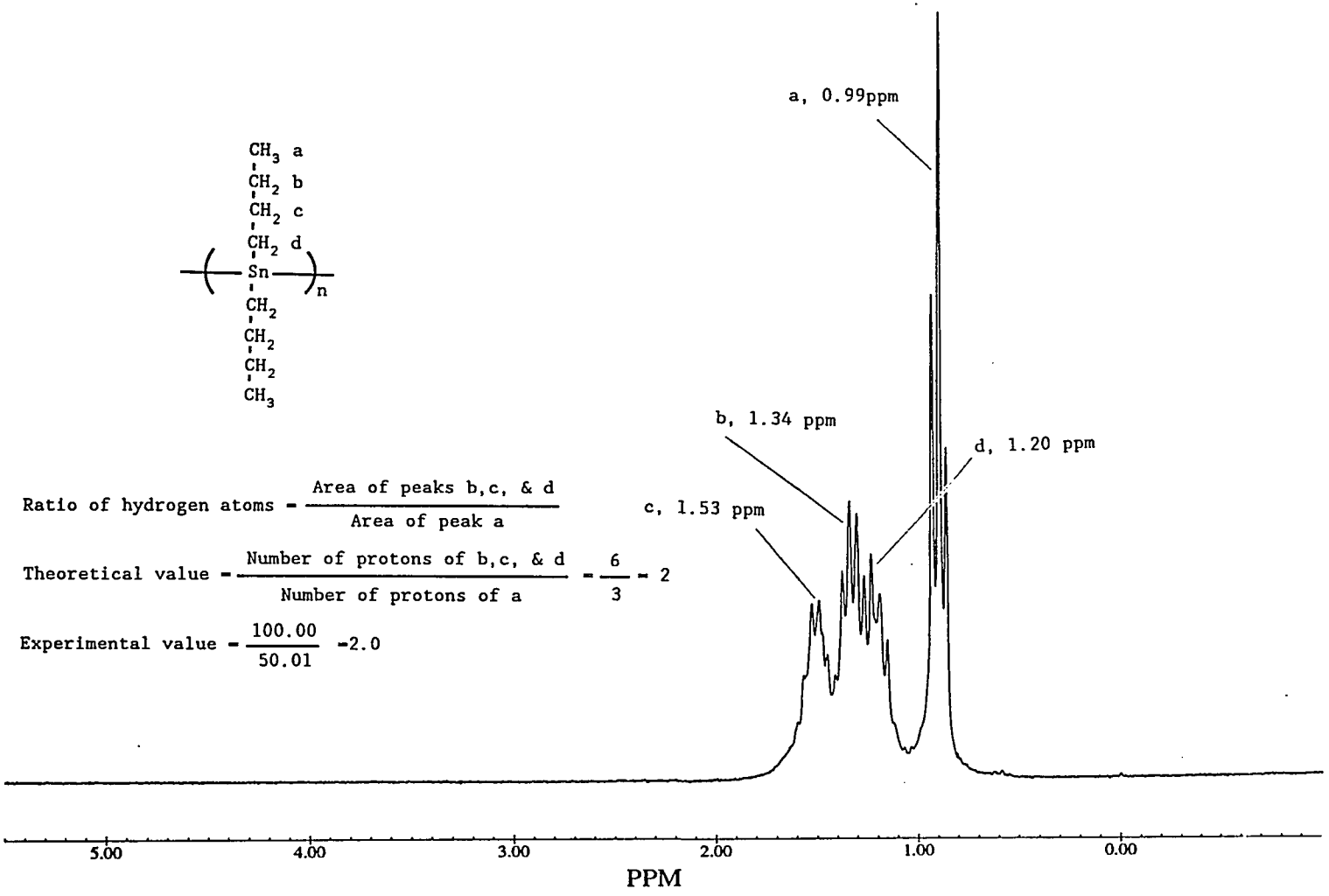


Fig. 2-1 ^{1}H NMR spectrum of polydibutylstannane in $CDCl_3$.

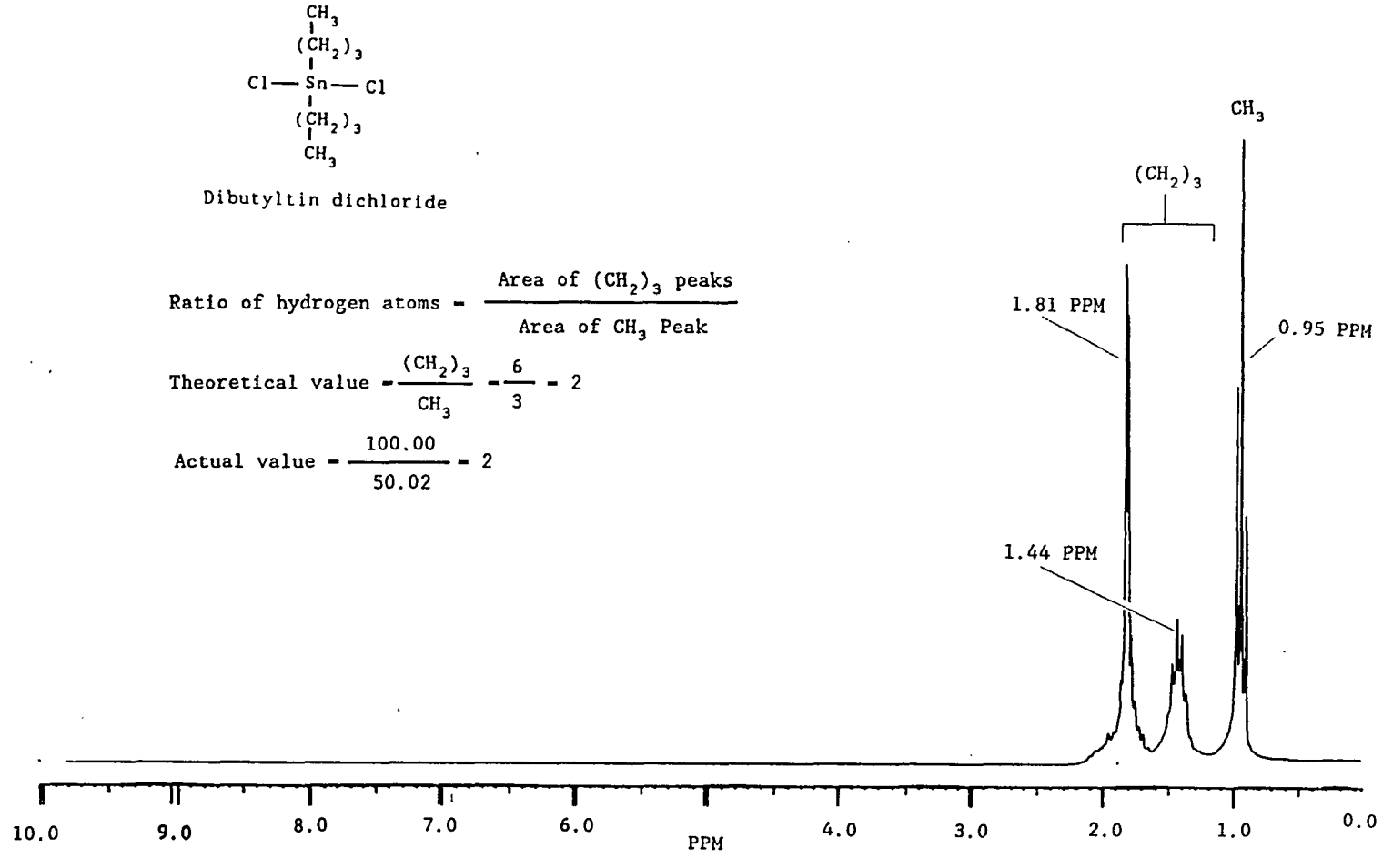


Fig. 2-2 ^{1}H NMR spectrum of dibutyltin dichloride in $CDCl_3$.

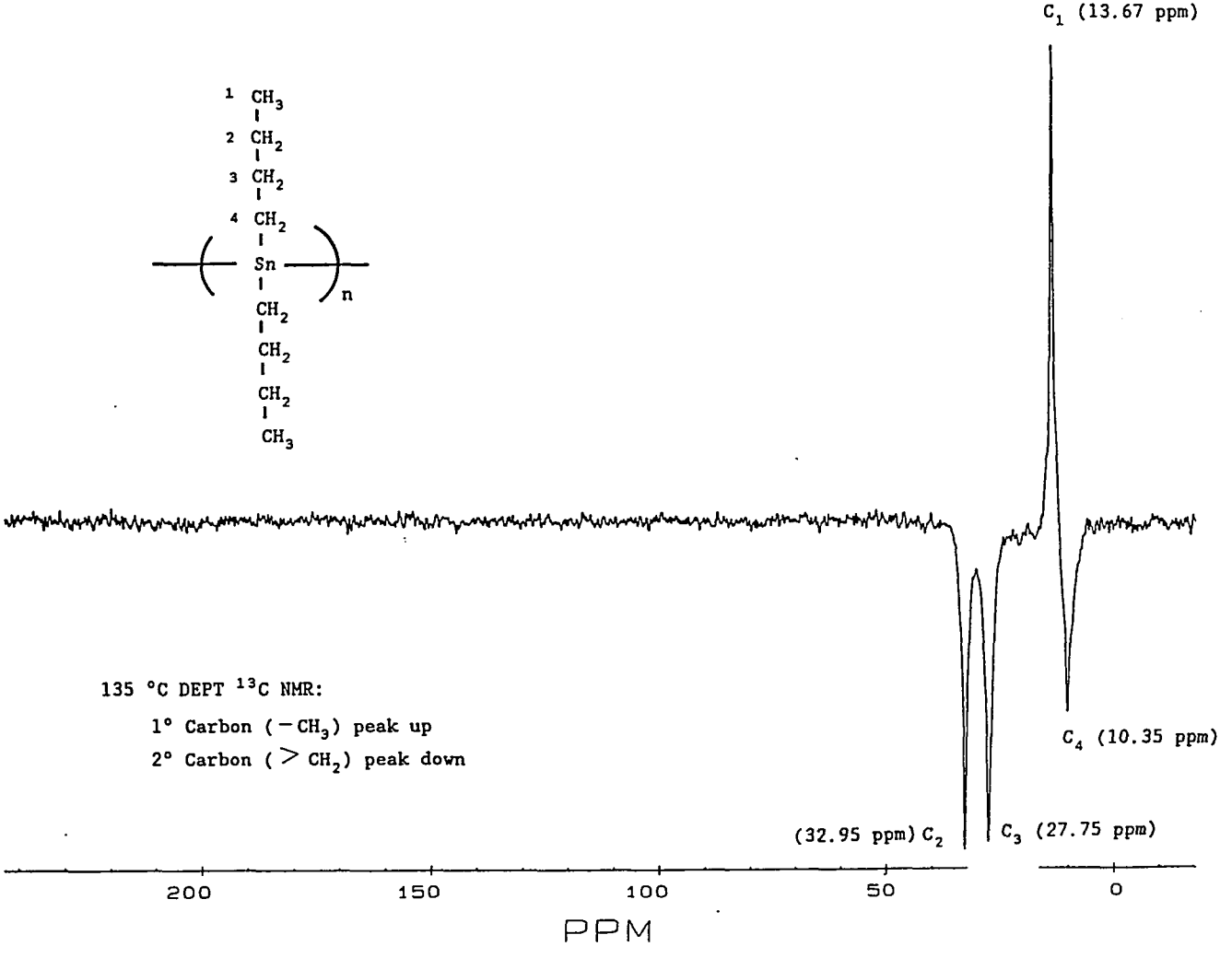


Fig. 2-3 DEPT NMR spectrum of polydibutylstannane in $CDCl_3$.

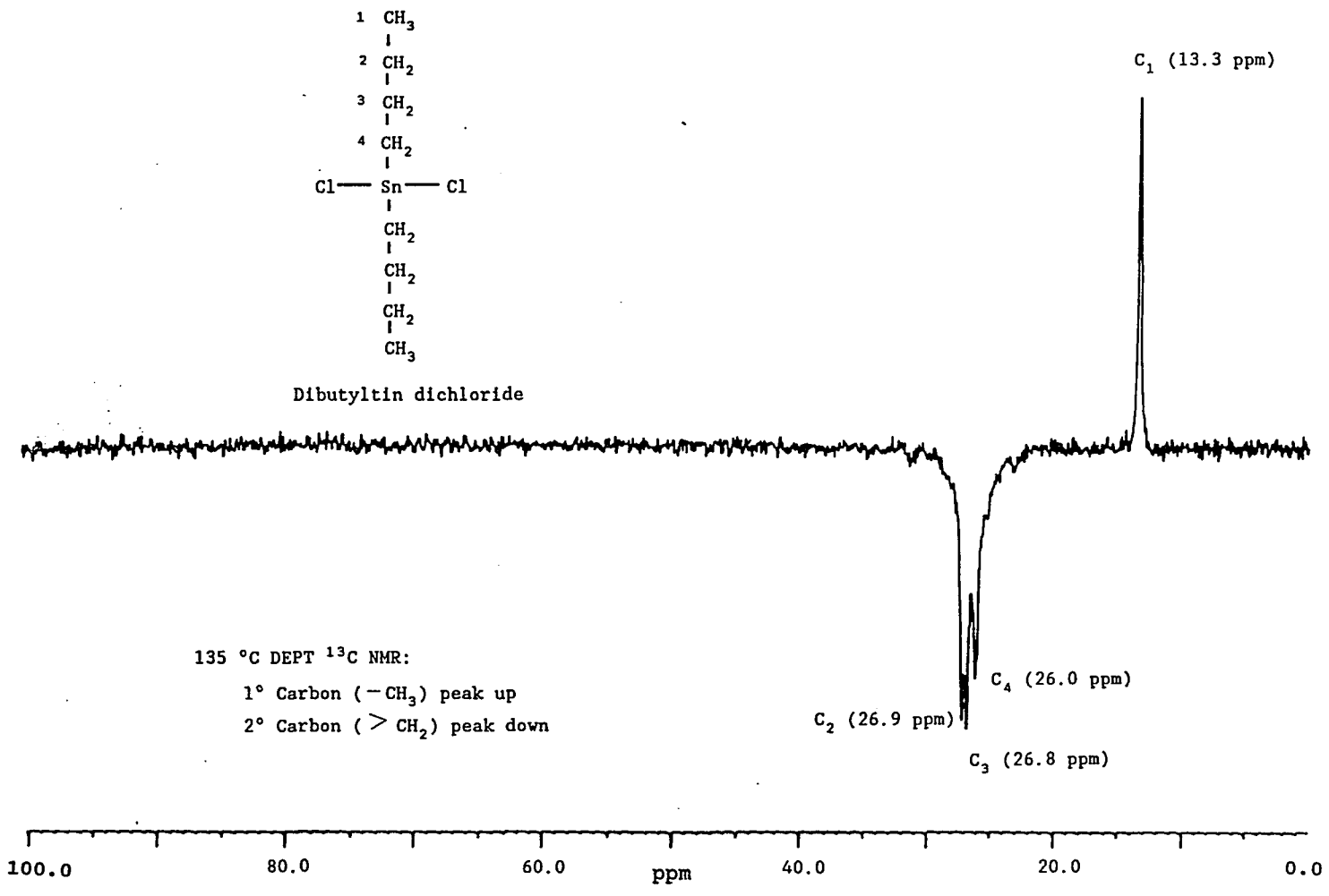


Fig. 2-4 DEPT NMR spectrum of dibutyltin dichloride in $CDCl_3$.

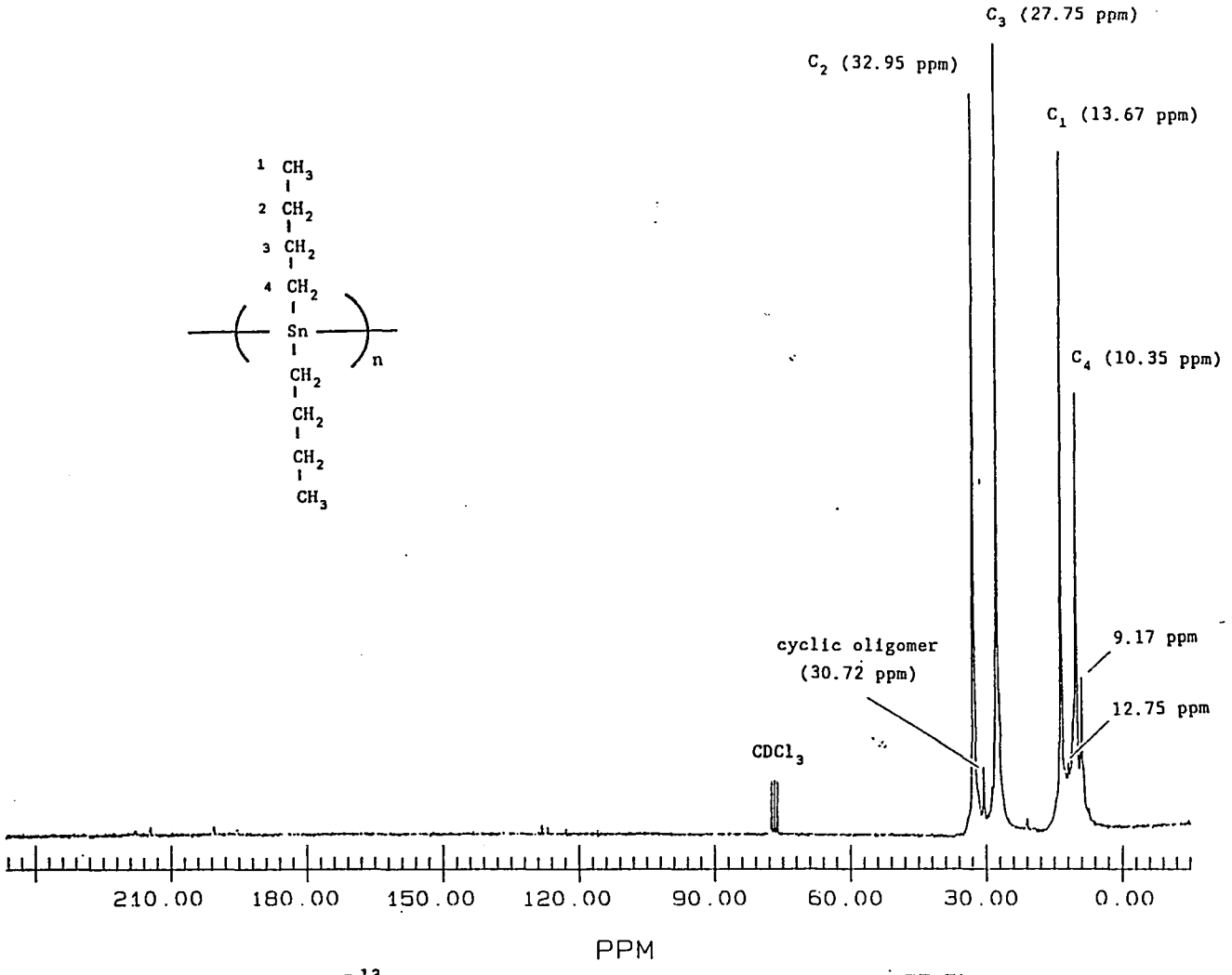


Fig. 2-5 ^{13}C NMR spectrum of polydibutylstannane in $CDCl_3$.

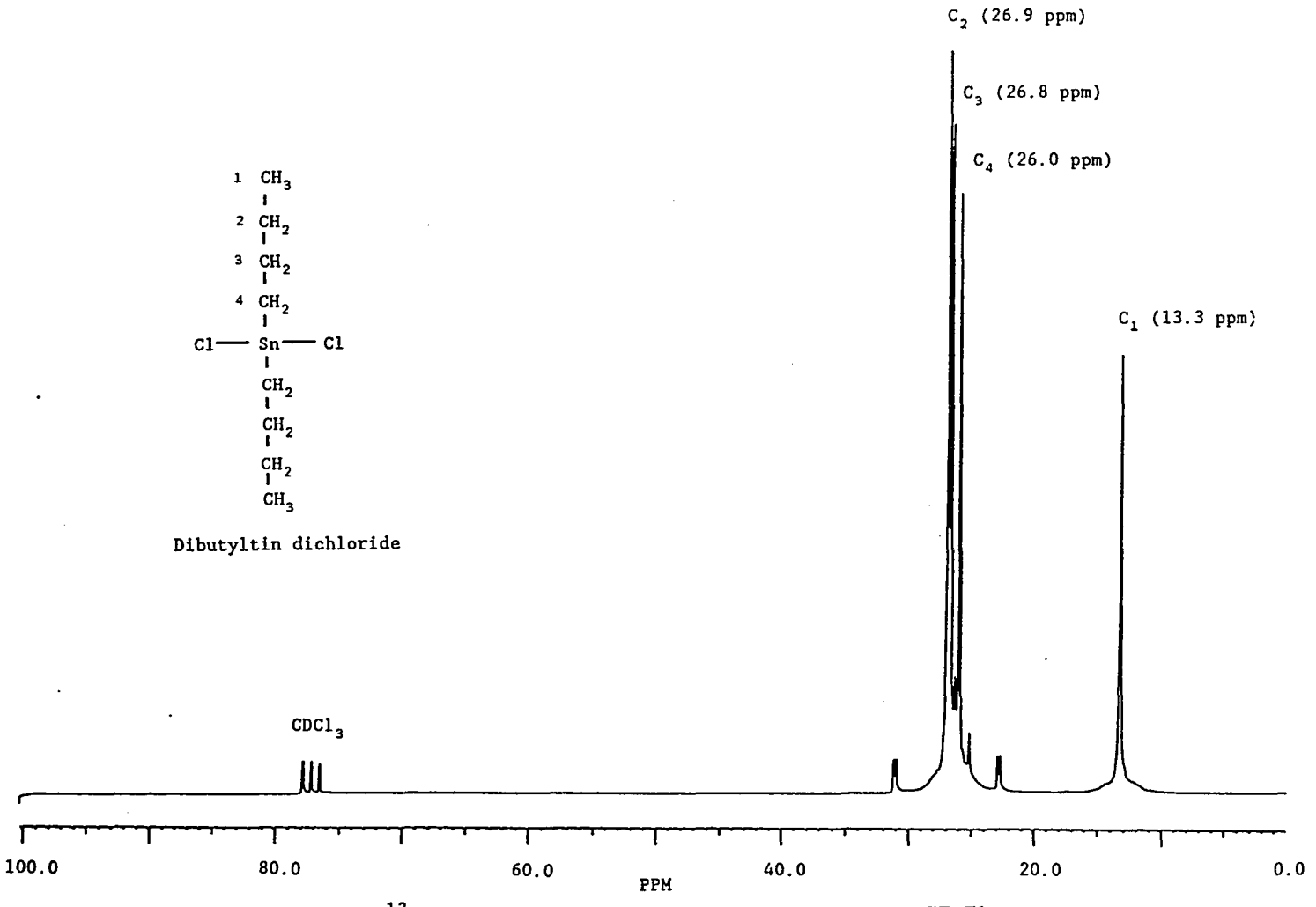


Fig. 2-6 ^{13}C NMR spectrum of dibutyltin dichloride in $CDCl_3$.

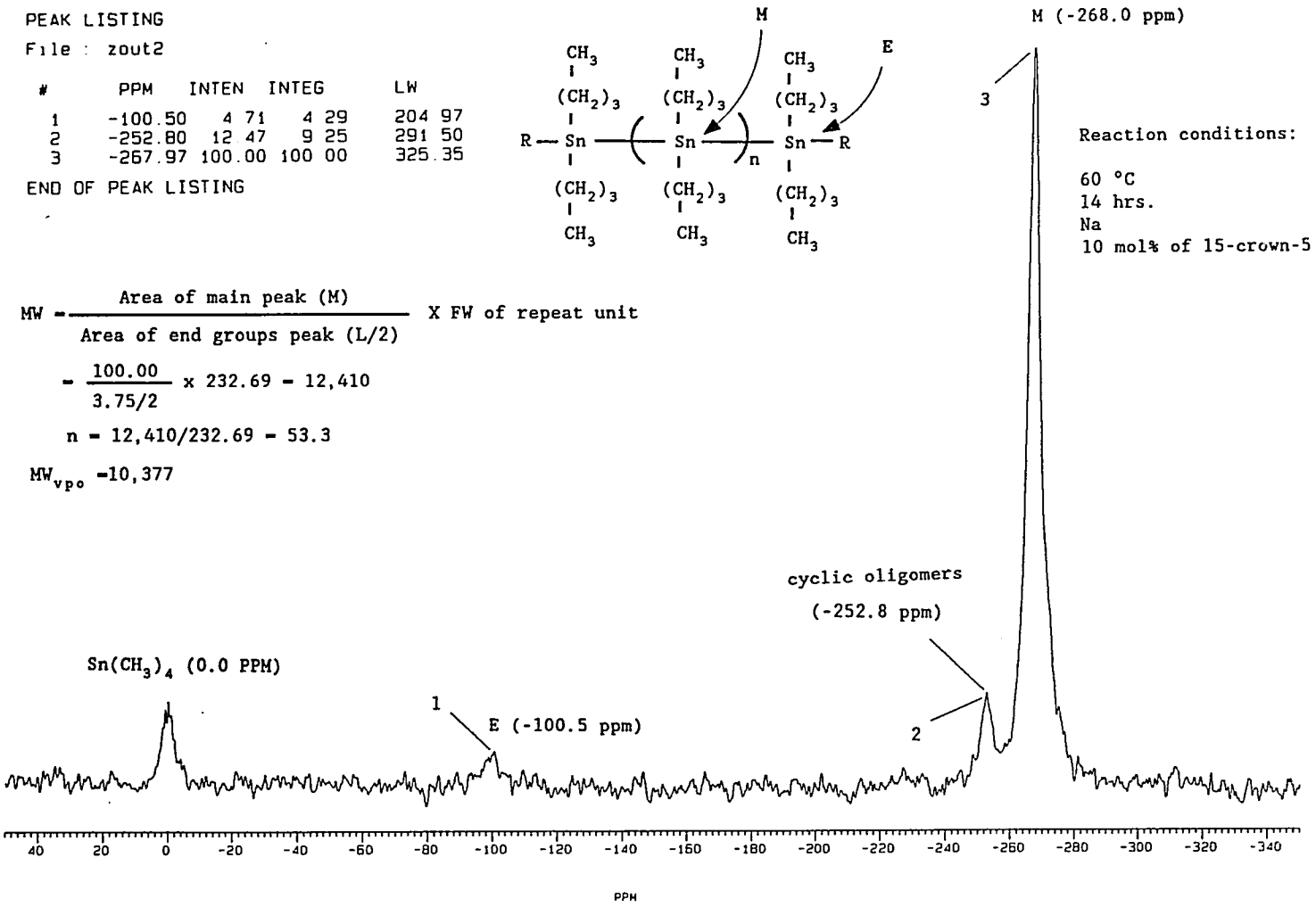
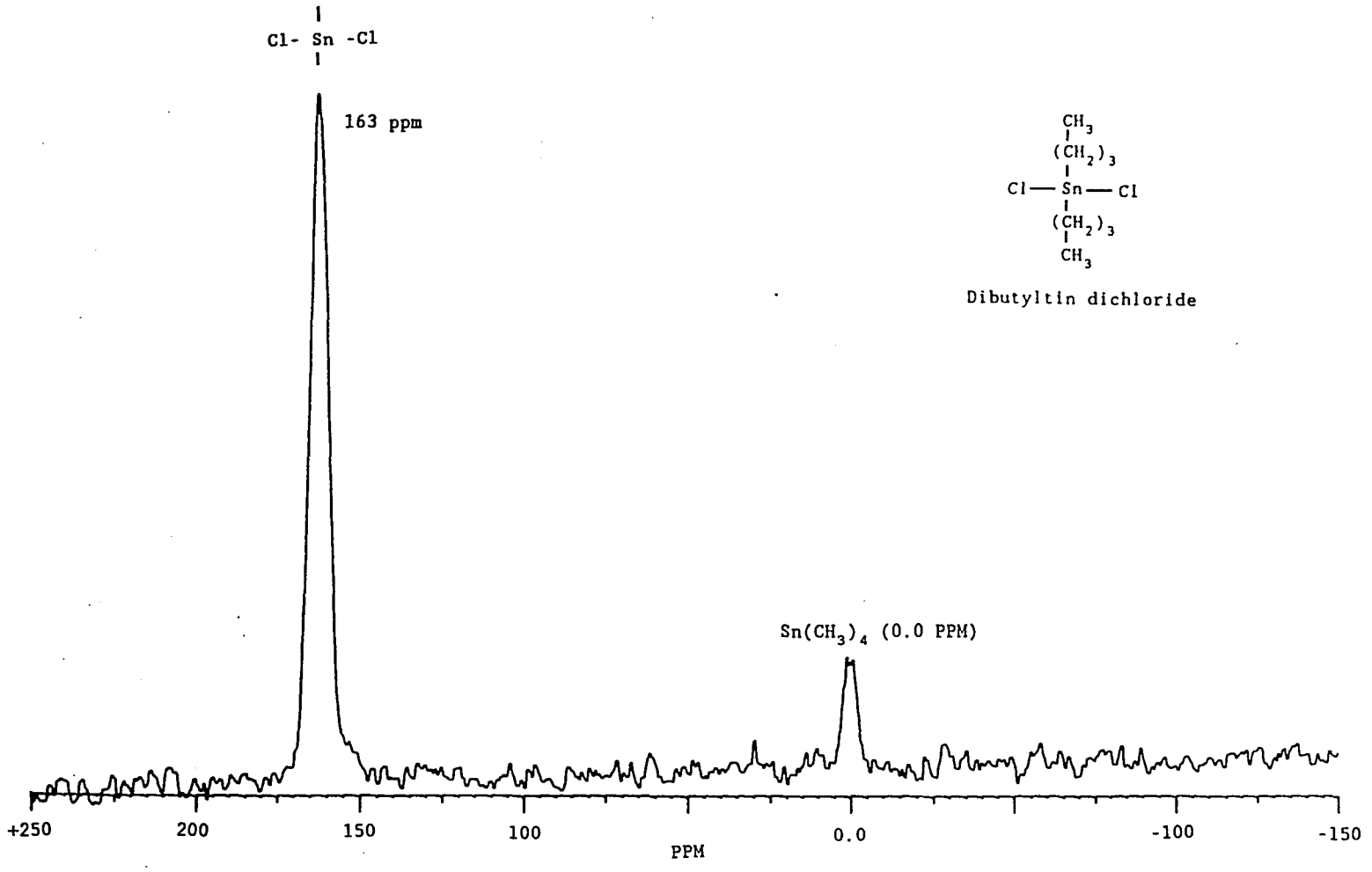


Fig. 2-7 ^{119}Sn NMR spectrum of polydibutylstannane in $CDCl_3$.



Dibutyltin dichloride

Fig. 2-8 ^{119}Sn NMR spectrum of dibutyltin dichloride in $CDCl_3$.

2.3.3. Synthesis of Polymer

The results on the polymerization of dibutyltin dichloride under a variety of reaction conditions are summarized in Table 2-2. This study has led to some interesting observations:

(i) The polymerization of dibutyltin dichloride is dramatically affected by reaction temperatures. Unlike polymerization for the preparation of polysilanes and polygermanes in refluxing solvent (generally toluene, at 110°C), dibutyltin dichloride does not polymerized at temperature above 100 °C without an additive (15-crown-5 or diglyme). Figure 2-9 (Table 2-2, exp. #1) shows a ^{119}Sn NMR spectrum of a typical reaction mixture. There are no polymer formed under these reaction conditions. As observed in Figure 2-10 (Table 2-2, exp.#2), the use of 15-crown-5 as an additive improved the yield of polymer (see Fig. 2-9 for comparison), but still resulting in higher than 40 % formation of cyclic oligomer during the synthetic process. Unlike for the case of polysilanes or polygermanes, polystannanes could not be formed at this temperature level. This may be due to the rate of thermal decomposition exceeding the rate of chain growth during the reaction at high temperature. Tin homonuclear chains may be too temperature sensitive in the solution with Na present and therefore never form high molecular polymer at high temperature.

Table 2-2. Summarizes the results of synthesis of polydibutylstannane under a variety of reaction conditions

Exp.#	Temp. (°C)	Time (hr)	Alkali Metal	Additive	Molecular Weight		cyclic oligomer (%)[e]	Fig. #
					^{119}Sn NMR	VPO		
1	108[a]	1	Na[b]	15-crown-5[c]	very low	——	≥ 40	2-9
2	108[a]	1	Na[b]	none	no reaction	——	——	2-10
3	80	6	Na[b]	15-crown-5[c]	4,021	——	——	2-14
4	80	6	K[d]	15-crown-5[c]	3,518	——	38.4	2-21
5	80	6	K[d]	none	no reaction	——	——	2-19
6	70	2.5	Na[b]	15-crown-5[c]	4,256	——	——	2-15
7	70	8	Na[b]	15-crown-5[c]	4,165	3,685	——	2-16
8	70	22	Na[b]	15-crown-5[c]	3,487	1,539	15.0	2-17
9	60	14	Na[b]	none	no reaction	——	——	2-20
10	60	14	Na[b]	15-crown-5 (10 mol%)	12,410	10,377	8.5	2-7
11	60	14	Na[b]	15-crown-5[c]	8,448	7,574	8.3	2-11
12	60	40	Na[b]	15-crown[c] (10 mol%)	8,448	6,892	11.8	2-12
13	60	14	Na[b]	diglyme[f]	6,271	4,436	20.1	2-13
14	50	40	Na[b]	15-crown-5[c]	no reaction	——	——	2-18
15[c]	60	14	Na[b]	15-crown-5[c]	——	——	——	2-22

(a) Refluxing temperature.

(b) 2.05 times moles of monomer used.

(c) 5 moles % based on amount of alkali metal used.

(d) 2.05 times moles of monomer used.

(e) % of cyclic oligomers determined by ^{119}Sn NMR spectrum using following equation:

$$\text{cyclic oligomer \%} = \frac{\text{area of cyclic oligomers peak}}{\text{total area of cyclic oligomers and polymer peaks}} \times 100\%$$

(f) 15 % based on volume of solvent used.

* ——— - not determined

(ii) Lower reaction temperatures favor high molecular weight. Decreasing the reaction temperature to 60 °C leads to significant improvement. Molecular weight of polymer up to $\overline{Mn} = 12.0 \times 10^3$ was obtained. Cyclic oligomers formed during synthetic process were reduced to only about 8.5 % (Fig. 2-7). This quantity approaches the yield of cyclic oligomers produced in typical sodium coupling reactions for polysilanes. A comparison of Figure 2-7 with 2-11 shows that increasing 15-crown-5 ether from 5 mol % to 10 mol % increases significantly the molecular weight from about $\overline{Mn} = 8 \times 10^3$ to $\overline{Mn} = 12 \times 10^3$.

(iii) The reaction time of 14 hours at 60 °C was found to be the best one for obtaining high molecular weight. Longer reaction time caused the degradation of the polymer to cyclic oligomers and low molecular weight linear oligomers at low level of monomer concentration due to the presence of excess sodium metal. An estimate of the

degradation level is shown in the Figure 2-12. Extending reaction time from 14 hours to 40 hours causes a molecular weight decrease from $\overline{Mn} = 12.0x10^3$ to about $\overline{Mn} = 8.0x10^3$. Cyclic oligomers increased from 8.5 % to 11.8 %. (Table 2-2, exp.#10 and #12).

(iv) The use of diglyme as a cosolvent resulted in significantly high yield of cyclic oligomers. Figure 2-13 (Table 2-2, exp. #13) shows the results of the ^{119}Sn NMR analysis. The molecular weight decreased from $\overline{Mn} = 12.0x10^3$ to $\overline{Mn} = 6.0x10^3$ when 15-crown-5 was replaced by diglyme under same reaction conditions. Cyclic oligomers detected increased from 8.5 % to 20.1 %.

(v) At the reaction temperature around 70-80 °C, less difference are observed. Molecular weights of polymer obtained were at the level of $\overline{Mn} = 4.0x10^3$ (Table 2-2, exp. #3, #6, #7, and #8, Figures 2-14, 2-15, 2-16, and 2-17). Similarly, extending reaction time from 2.5 hours to 22 hours at 70 °C causes a molecular weight decrease from $\overline{Mn} = 4.0x10^3$ to about $\overline{Mn} = 3.0x10^3$.

(vi) At the reaction temperature 50 °C or lower, polymerization does not occur (Table 2-2, exp. #14, Figure 2-18)

(vii) As shown on Table 2-2, (exp. #3-4, #6-8, and #10-13), dibutyltin dichloride could only be polymerized in the presence of an additive such as 15-crown-5 or diglyme. Polymerization does not occur without an additive at any temperatures (Table 2-2, exp. #1, #5, and #9, Figures 2-9, 2-19, and 2-20). The presence of crown ether or diglyme may

accelerate electron transfer due to an increased solvation of the alkali metal cation which is a product of the reaction, thus shifting the electron transfer equilibrium in favor of the formation of products.

(viii) Compared with sodium, more active potassium metal caused higher percentage of cyclic oligomers. As shown in the Figure 2-21, 38.4 % of cyclic oligomers was formed during this synthetic process. A possible explanation is that the high reactivity potassium may increase reactivity of stannyl anions radical and caused a back-biting (degradation) process which leads to cleavage Sn-Sn of bonds and formation of the cyclostannanes. The possible mechanism are discussed in Section 2.4 in details.

(ix) Purity of the dibutyltin dichloride monomer is a critical requirement to obtain high molecular weight polystannanes. Figure 2-22 shows the ^{119}Sn NMR spectrum of product obtained from experiment #15 using dibutyltin dichloride purchased from Aldrich (97 %). This spectrum indicates that no polymer was formed.

(x) As expected, this polymer was sensitive to oxygen in a solution. This was observed by stirring the polymer solution in an open NMR tube for 5 minutes, and then acquiring its ^{119}Sn NMR spectrum (Figure 2-23). Two new absorptions at -203 ppm and -229 ppm were observed (see Fig. 2-12 obtained with same polymer solution before exposing to oxygen for comparison). They were assigned to the <u>Sn</u> in (R-O-<u>Sn</u>-O-) chain, and <u>Sn</u> in (R-O-Sn-O-<u>Sn</u>-O-Sn-) chain, respectively. Both the structures were formed by the

oxygenation reaction of the oxygen sensitive Sn-Sn bonds. This was further confirmed by the spectra of two model compounds, dibutyltin dimethoxide, (Fig. 2-24) and poly(dibutyltin dimethoxide) (Fig. 2-25). The absorption of Sn in dibutyltin dimethoxide, $CH_3OSnBu_2OCH_3$, appears at -207 ppm. The absorptions of Sn in poly(dibutylstannoxide), $CH_3O(SnBu_2O)_nCH_3$, appeared at -203 ppm and -229 ppm for end group and backbone, respectively. Their assignments are shown in the Figure 2-25.

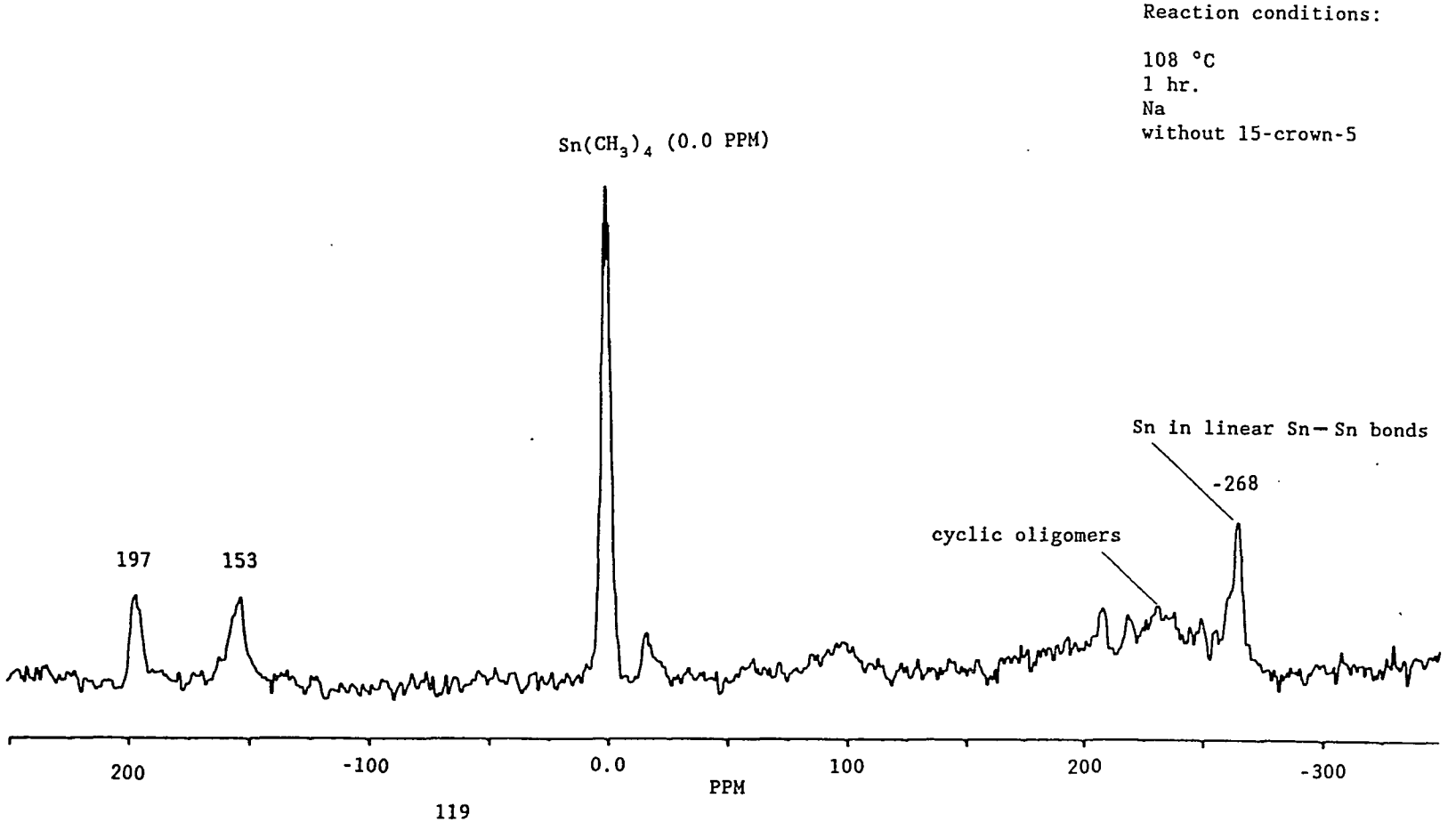


Fig. 2-9 ^{119}Sn NMR spectrum of reaction mixture of exp. #1 in $CDCl_3$.

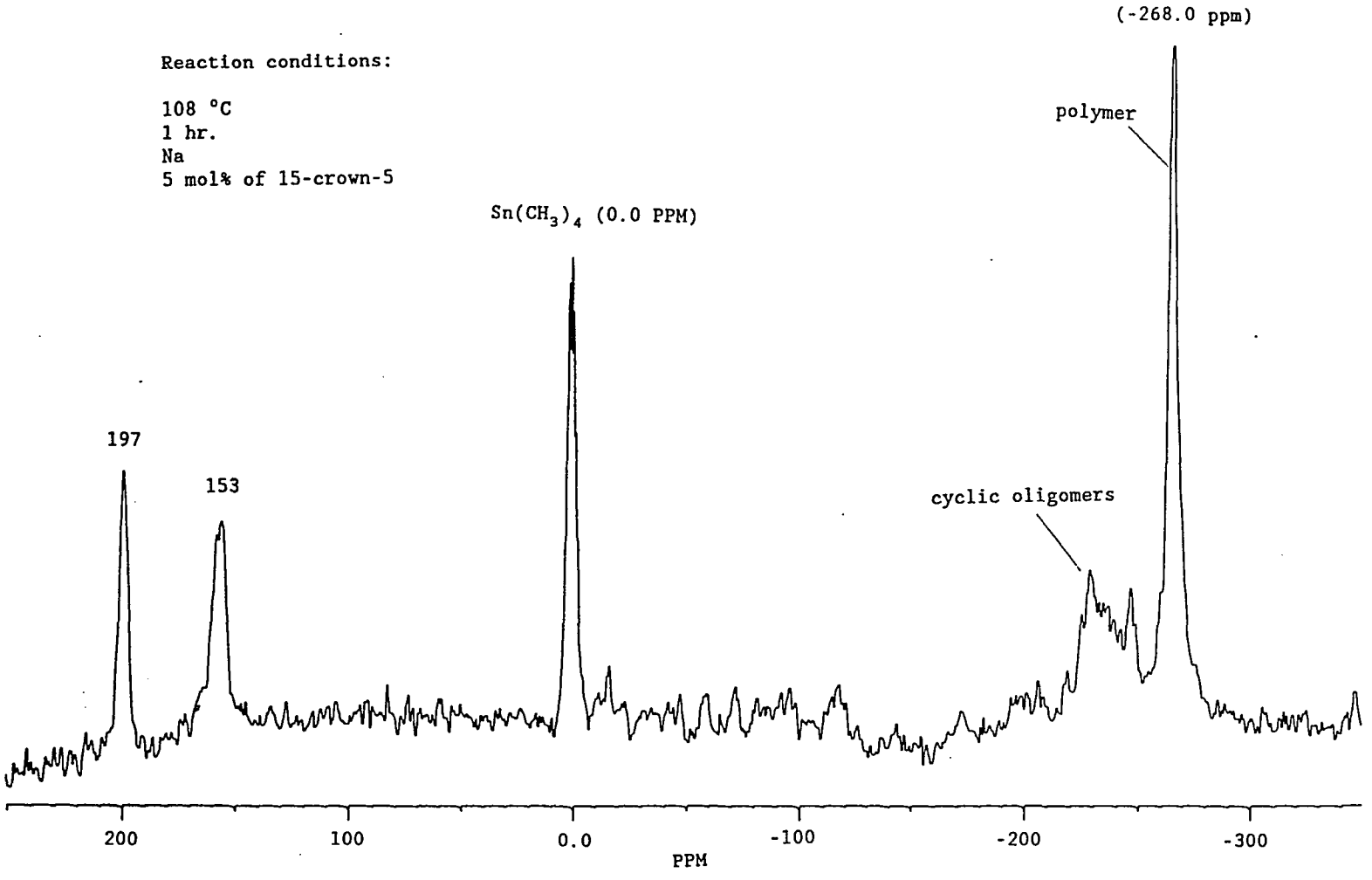


Fig. 2-10 ^{119}Sn NMR spectrum of reaction mixture of exp. #2 in $CDCl_3$.

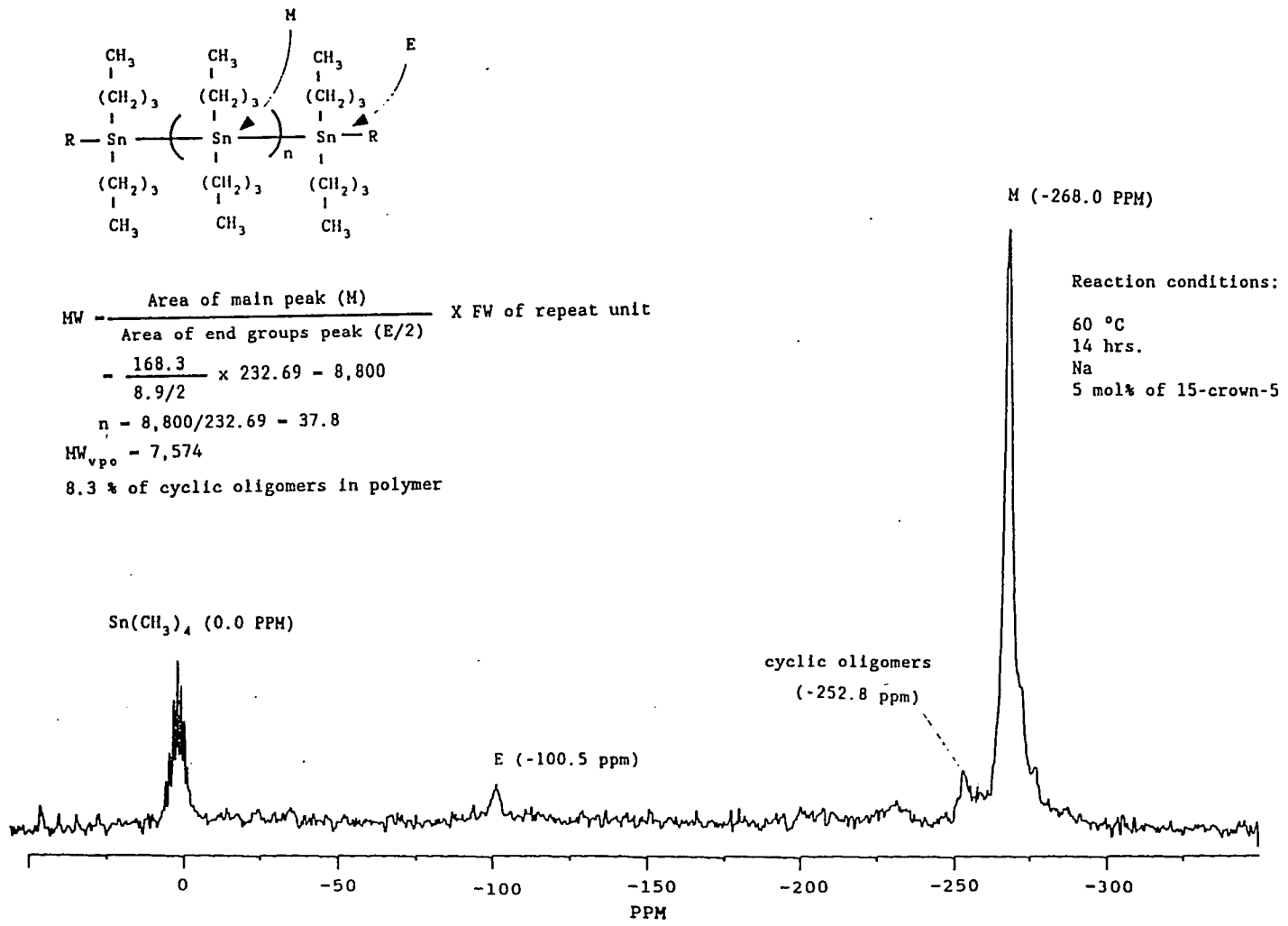


Fig. 2-11 ^{119}Sn NMR spectrum of polydibutylstannane (exp. #11) in $CDCl_3$.

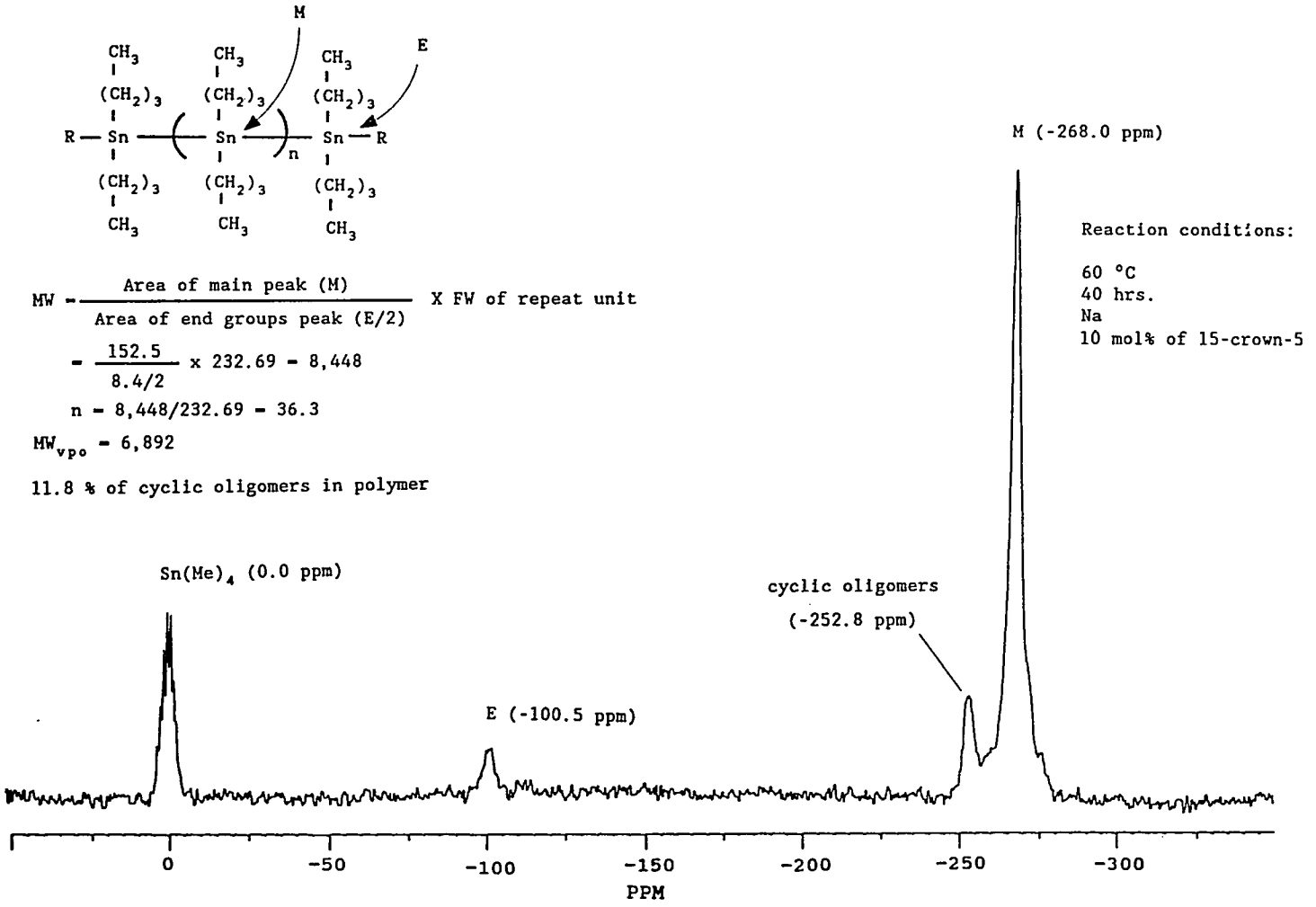


Fig. 2-12 ^{119}Sn NMR spectrum of polydibutylstannane (exp. #12) in $CDCl_3$.

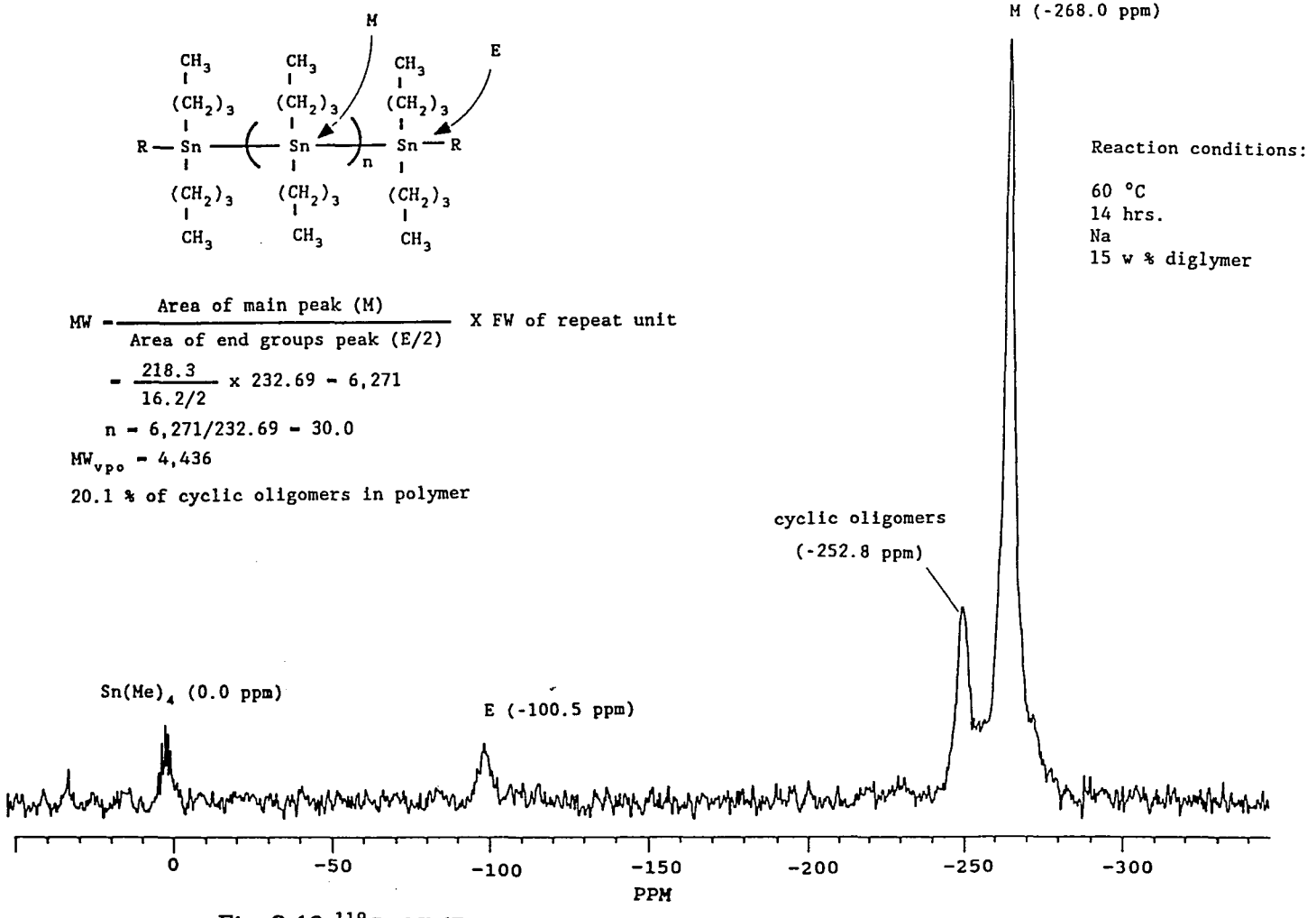


Fig. 2-13 ^{119}Sn NMR spectrum of polydibutylstannane (exp. #13) in $CDCl_3$.

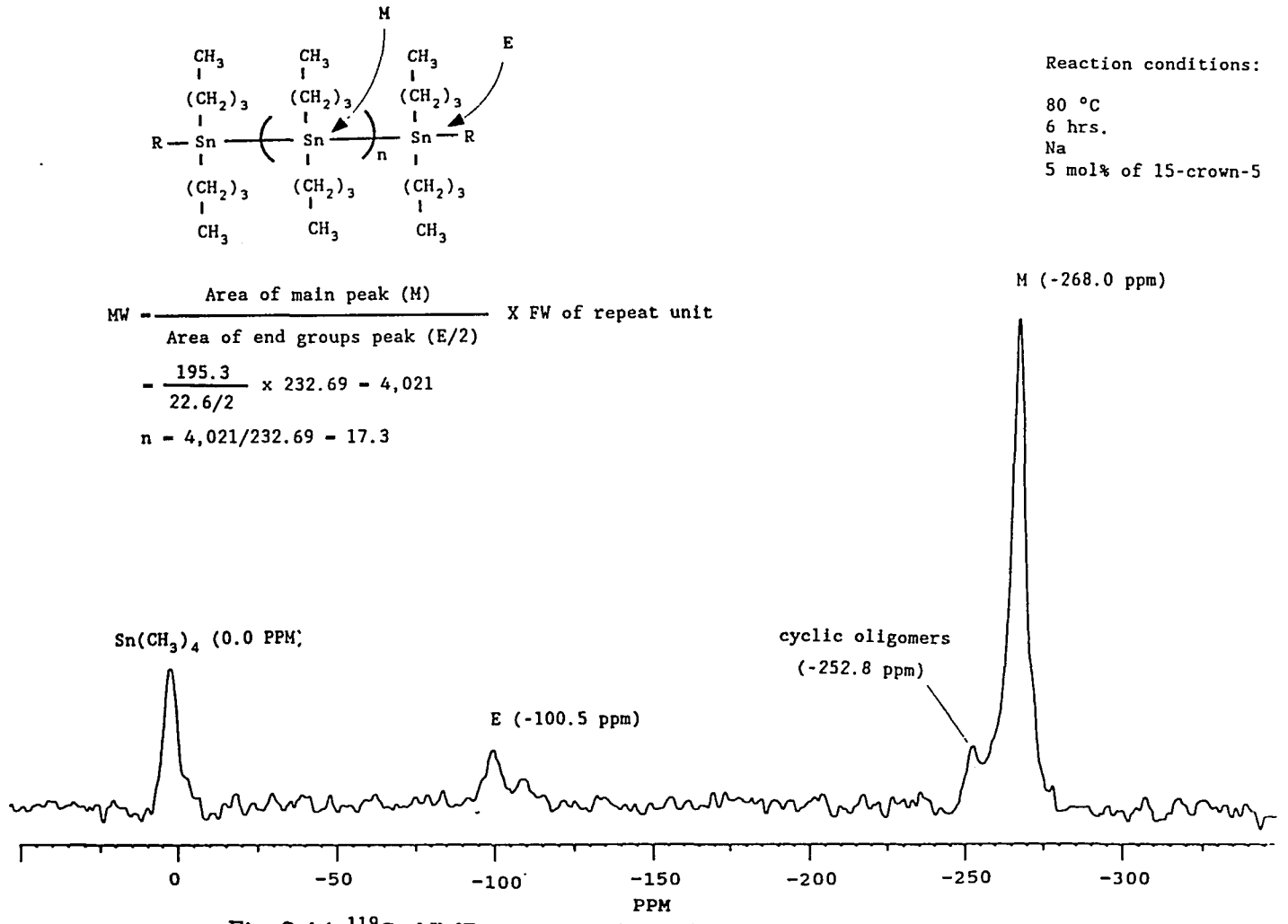


Fig. 2-14 ^{119}Sn NMR spectrum of polydibutylstannane (exp. #3) in $CDCl_3$.

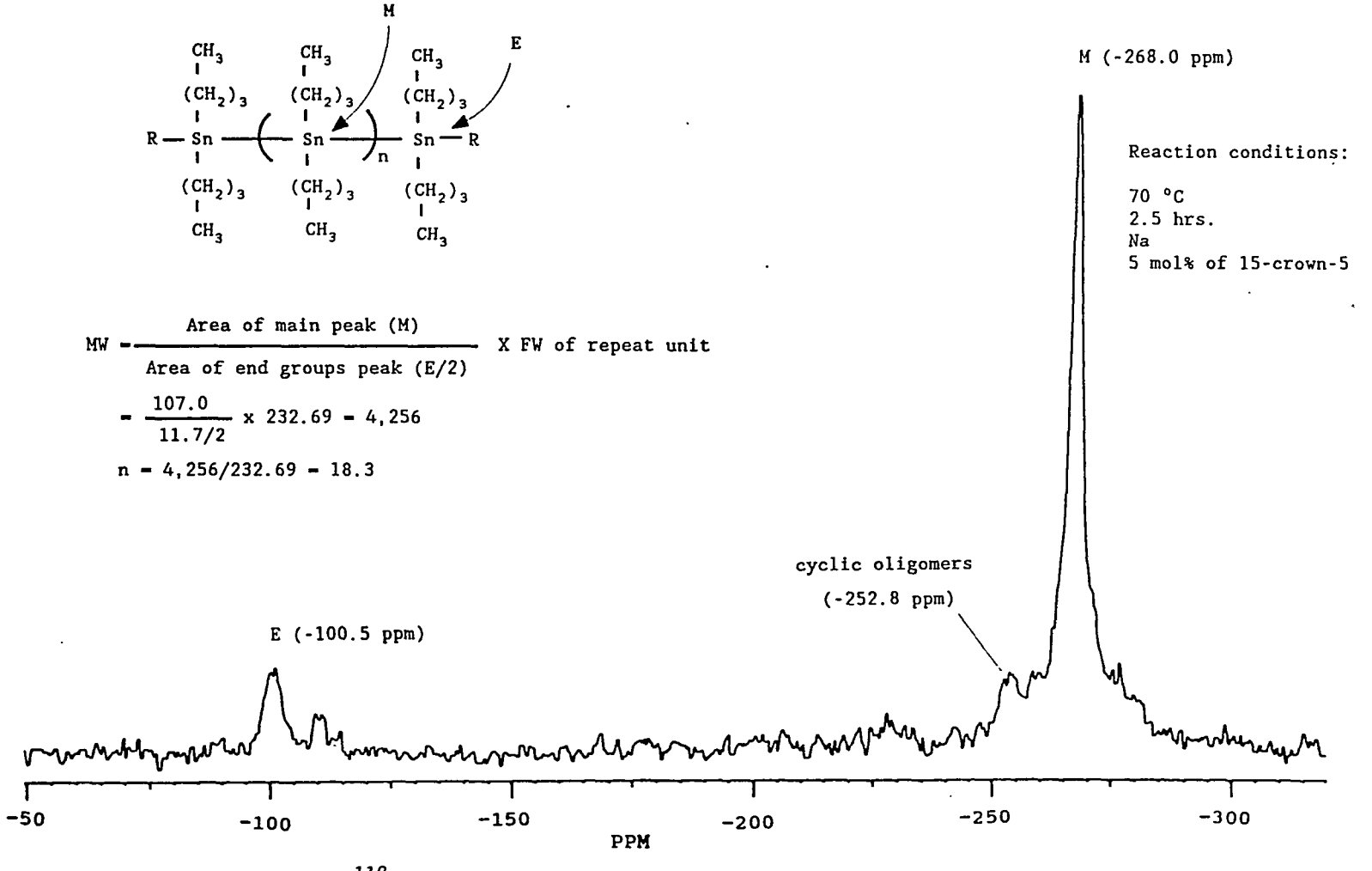


Fig. 2-15 ^{119}Sn NMR spectrum of polydibutylstannane (exp. #6) in $CDCl_3$.

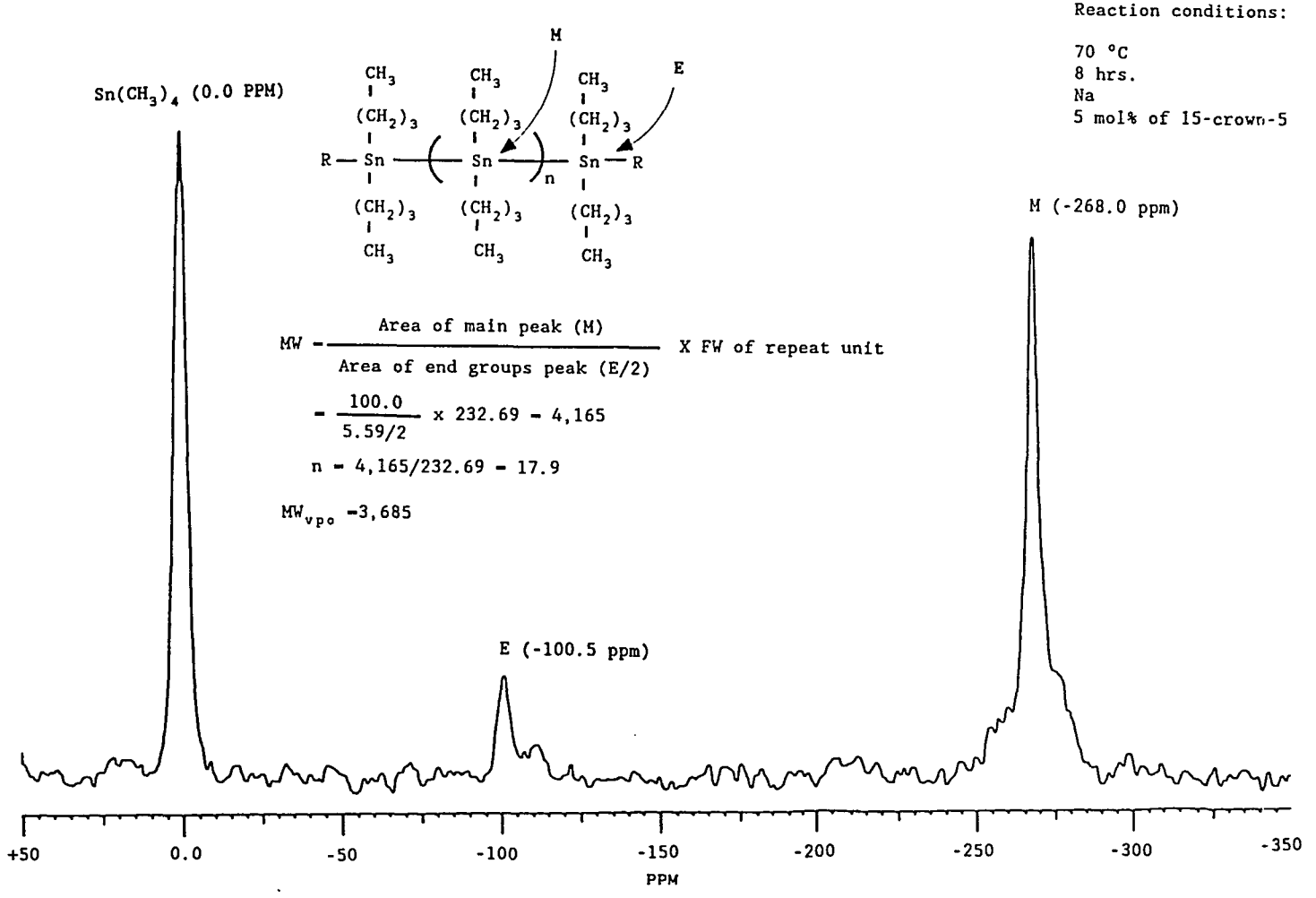


Fig. 2-16 ^{119}Sn NMR spectrum of polydibutylstannane (exp. #7) in $CDCl_3$.

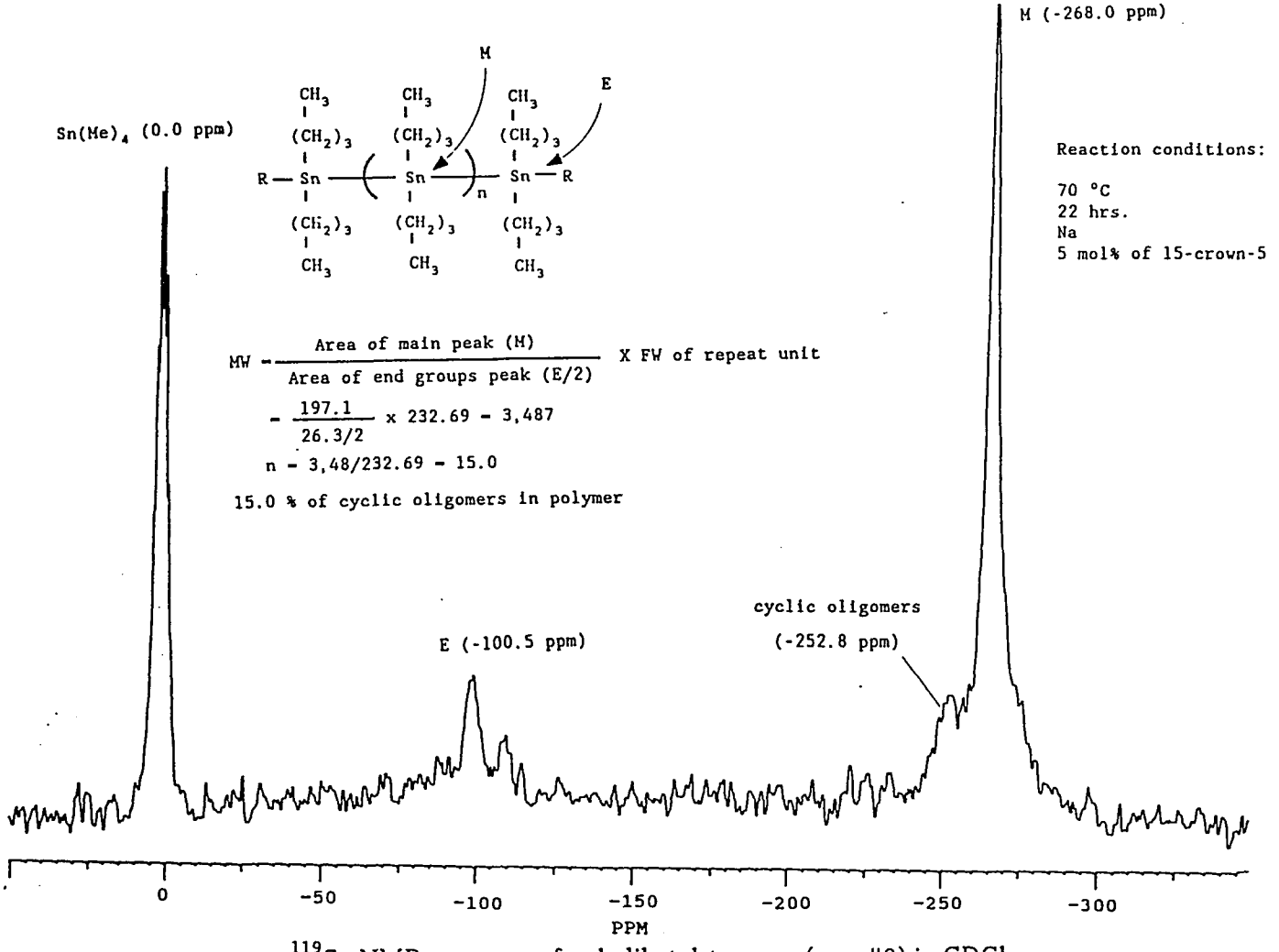


Fig. 2-17 ^{119}Sn NMR spectrum of polydibutylstannane (exp. #8) in $CDCl_3$.

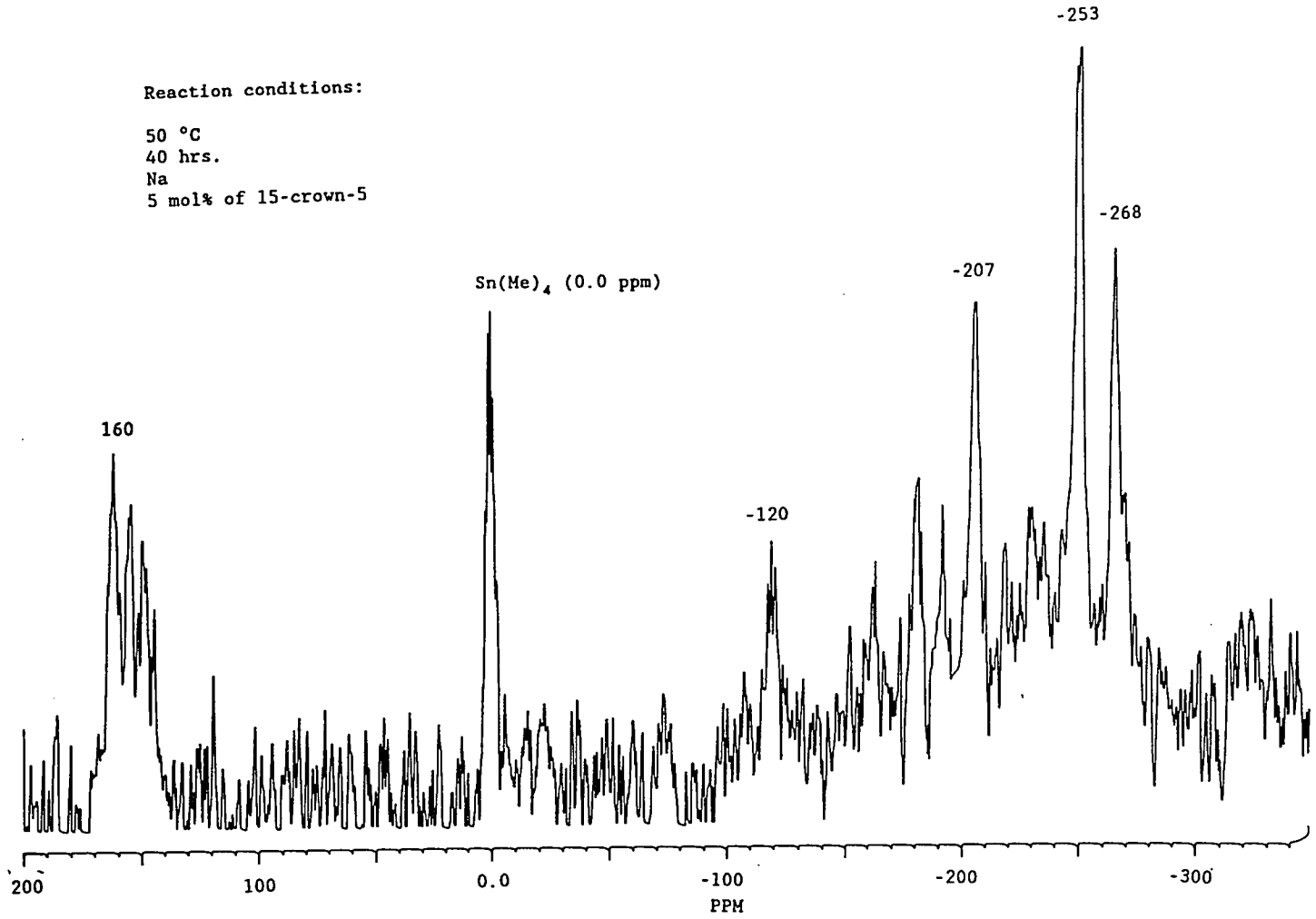


Fig. 2-18 ^{119}Sn NMR spectrum of reaction mixture of exp. #14 in $CDCl_3$.

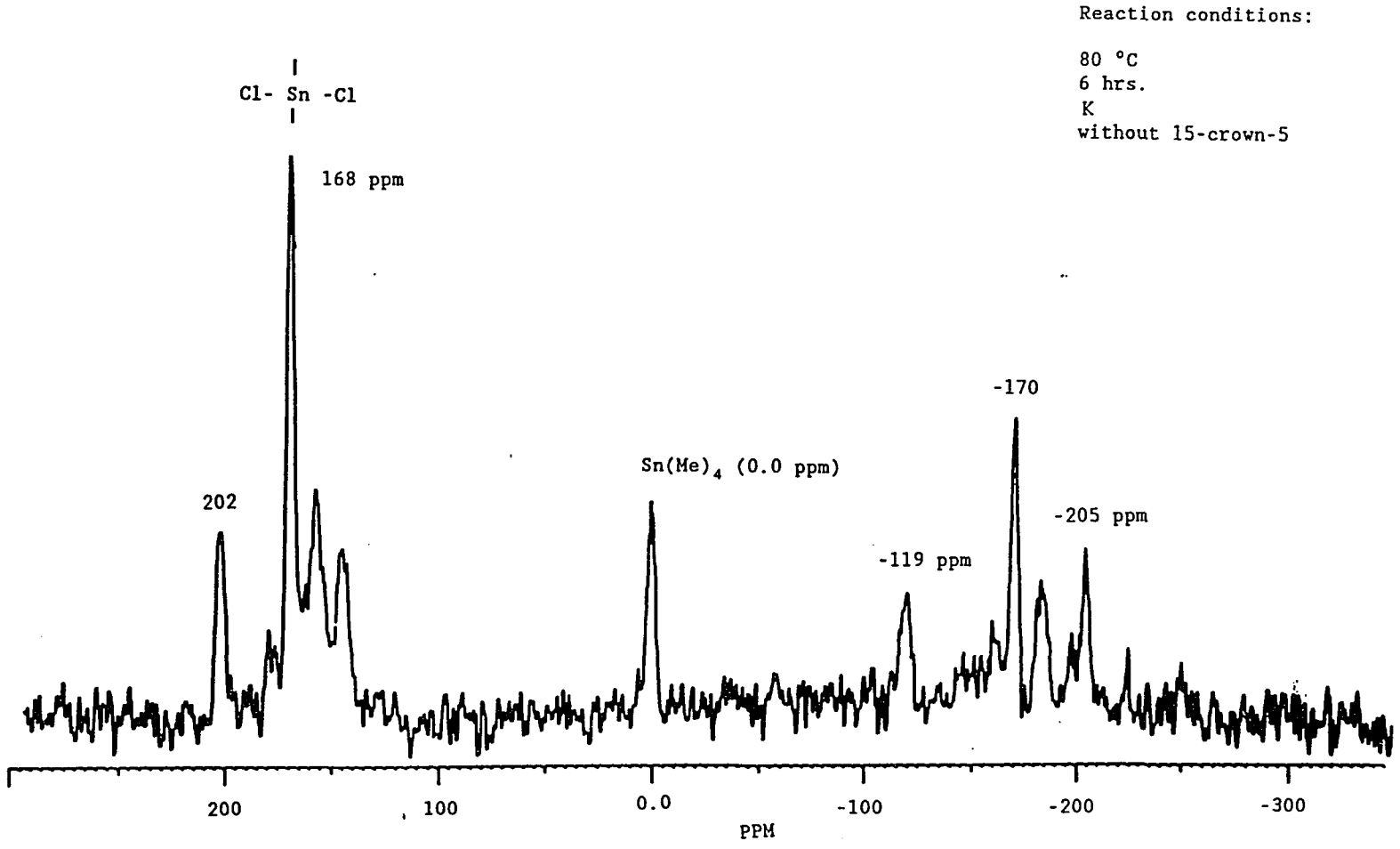


Fig. 2-19 ^{119}Sn NMR spectrum of reaction mixture of exp. #5 in $CDCl_3$.

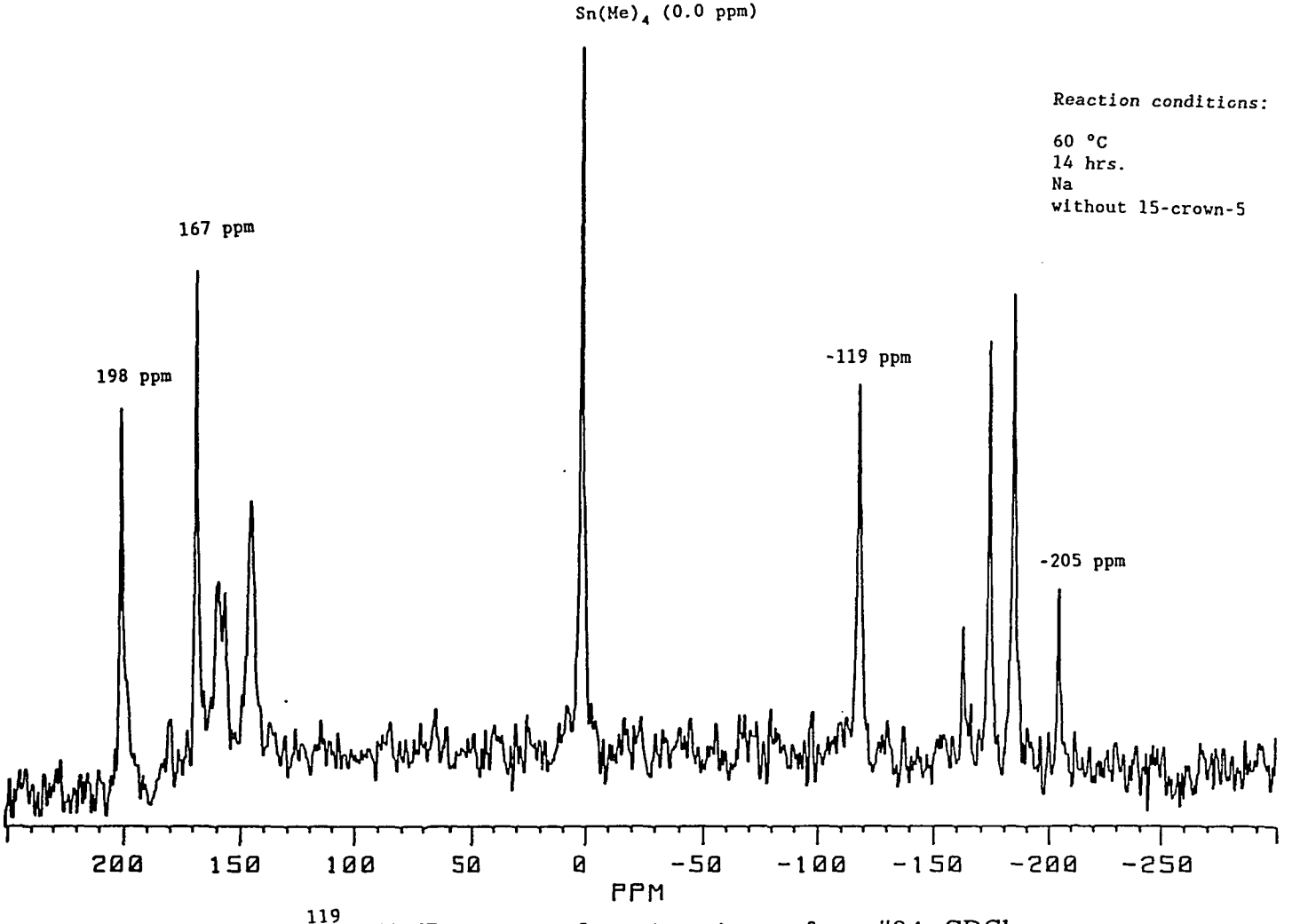


Fig. 2-20 ^{119}Sn NMR spectrum of reaction mixture of exp. #9 in $CDCl_3$.

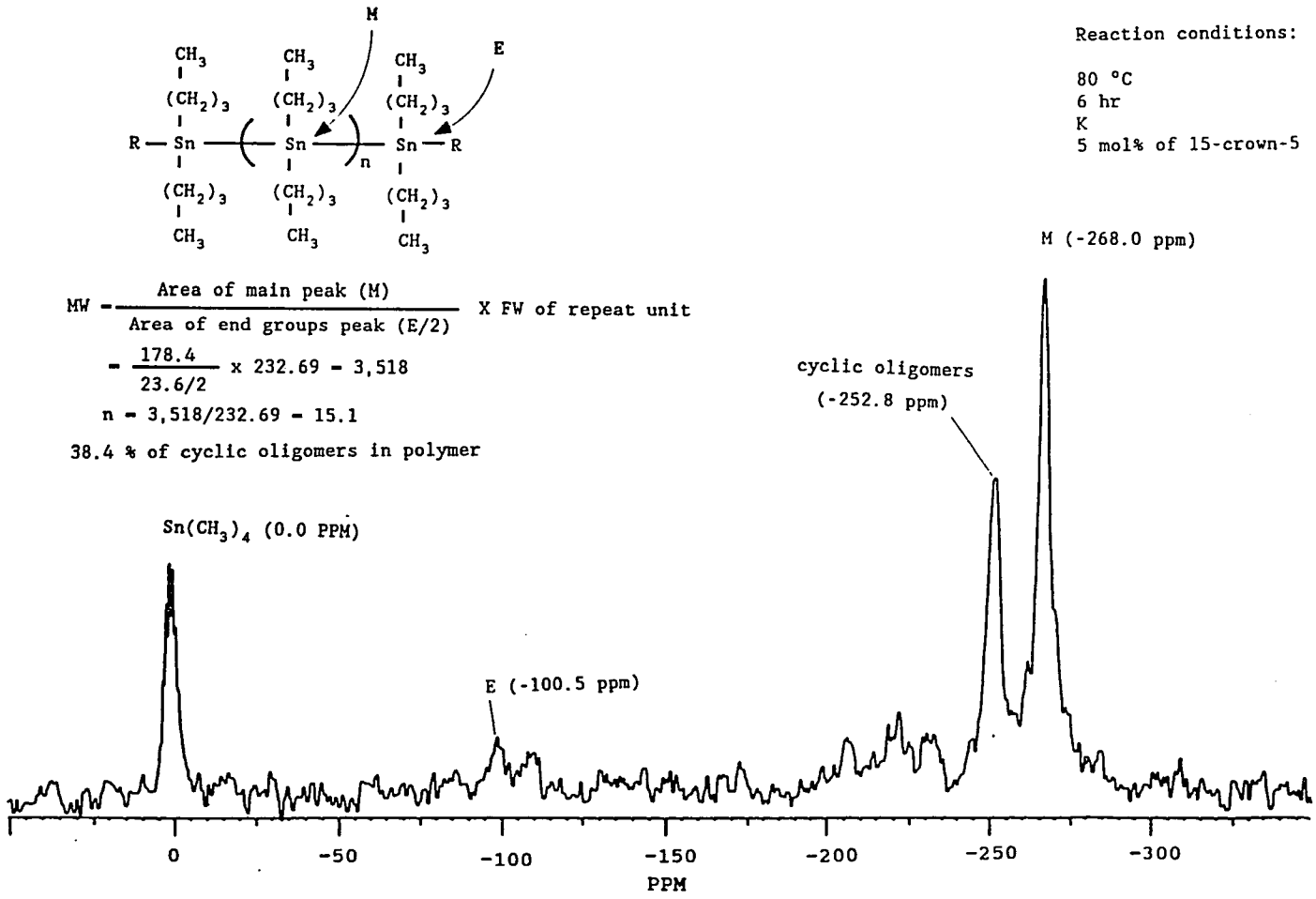


Fig. 2-21 ^{119}Sn NMR spectrum of polydibutylstannane (exp. #4) in $CDCl_3$.

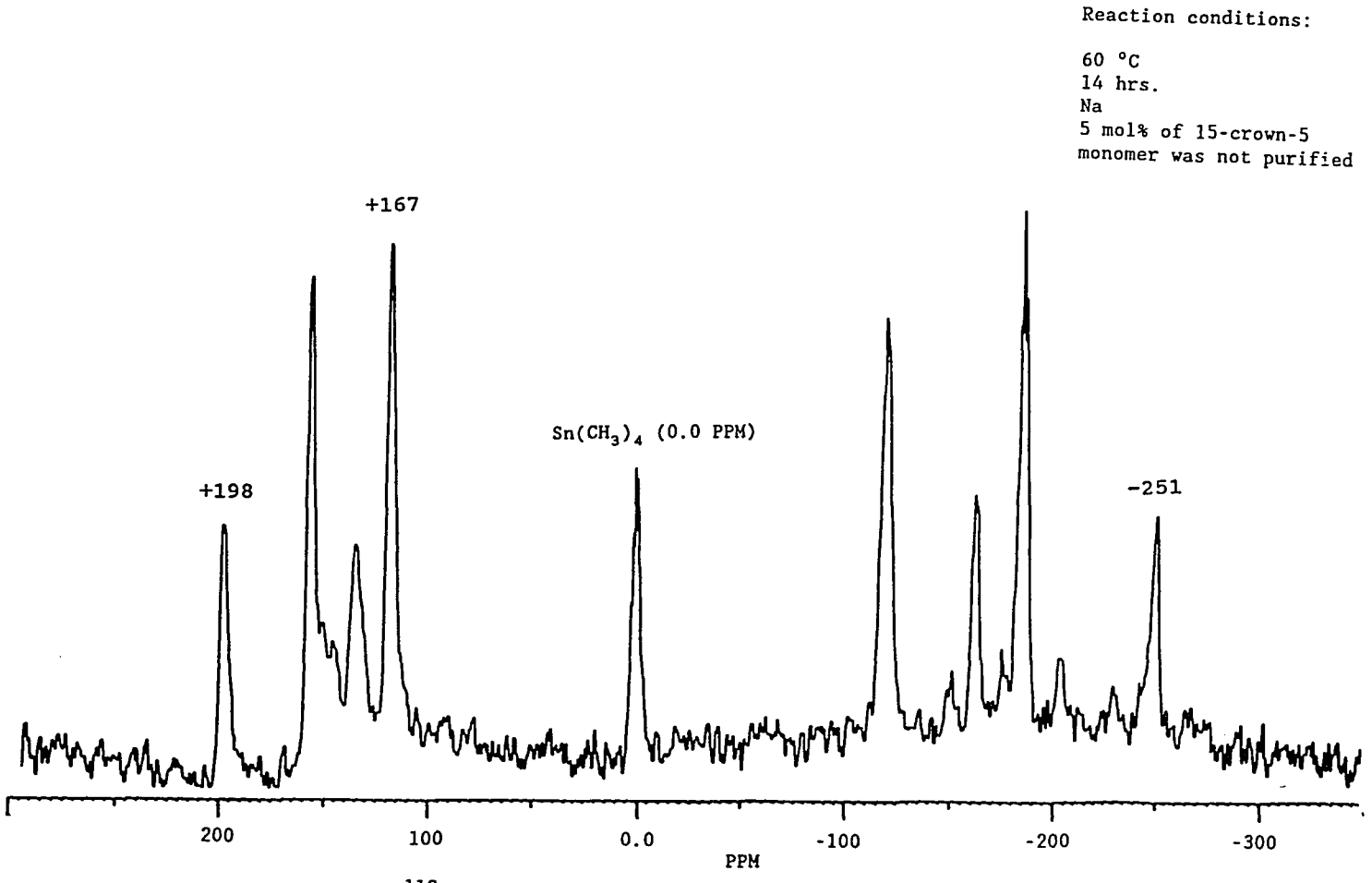


Fig. 2-22 ^{119}Sn NMR spectrum of reaction mixture of exp. #15 in $CDCl_3$.

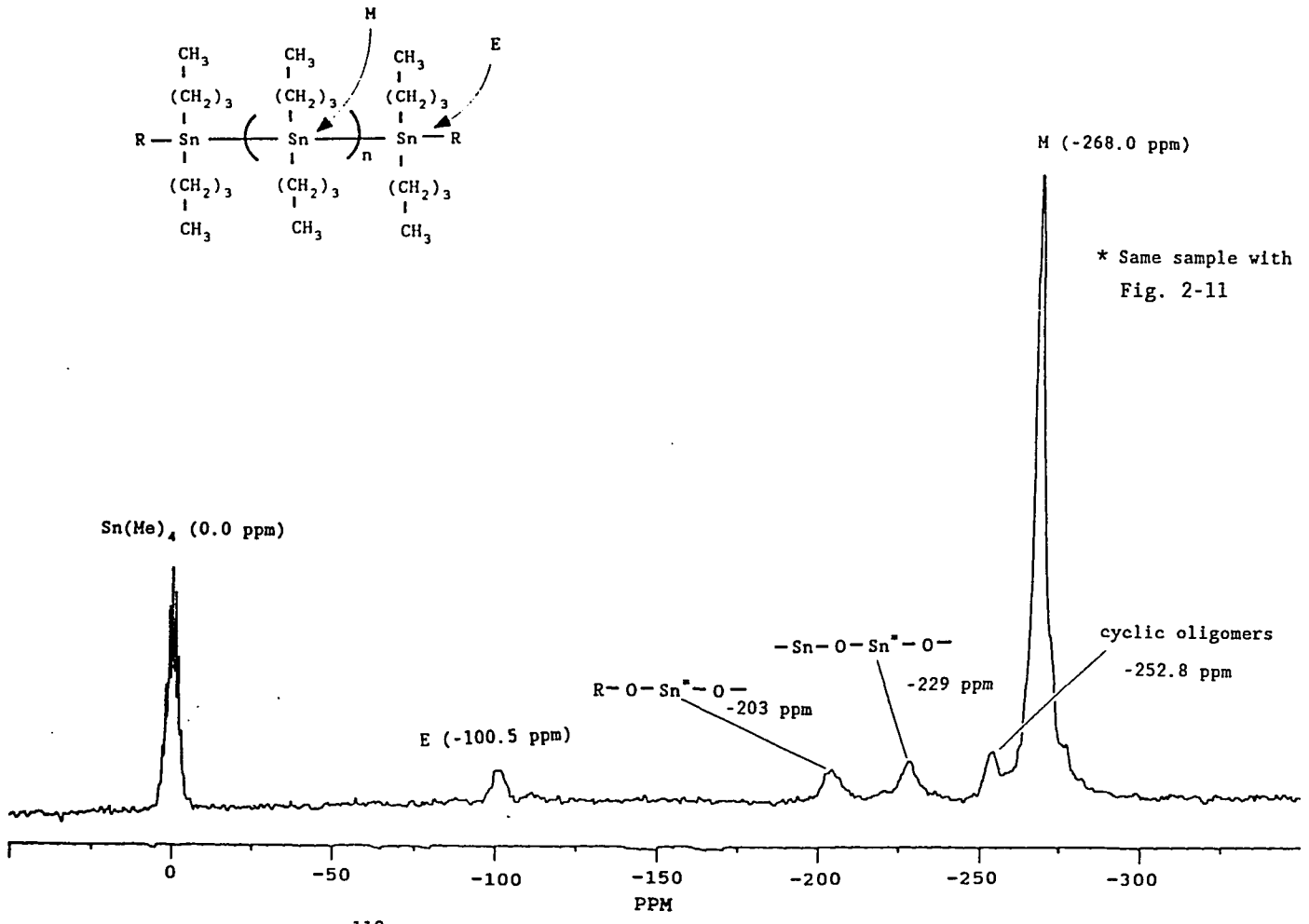


Fig. 2-23 ^{119}Sn NMR spectrum of polydibutylstannane* in $CDCl_3$ after stirring an open NMR tube for 5 minutes.

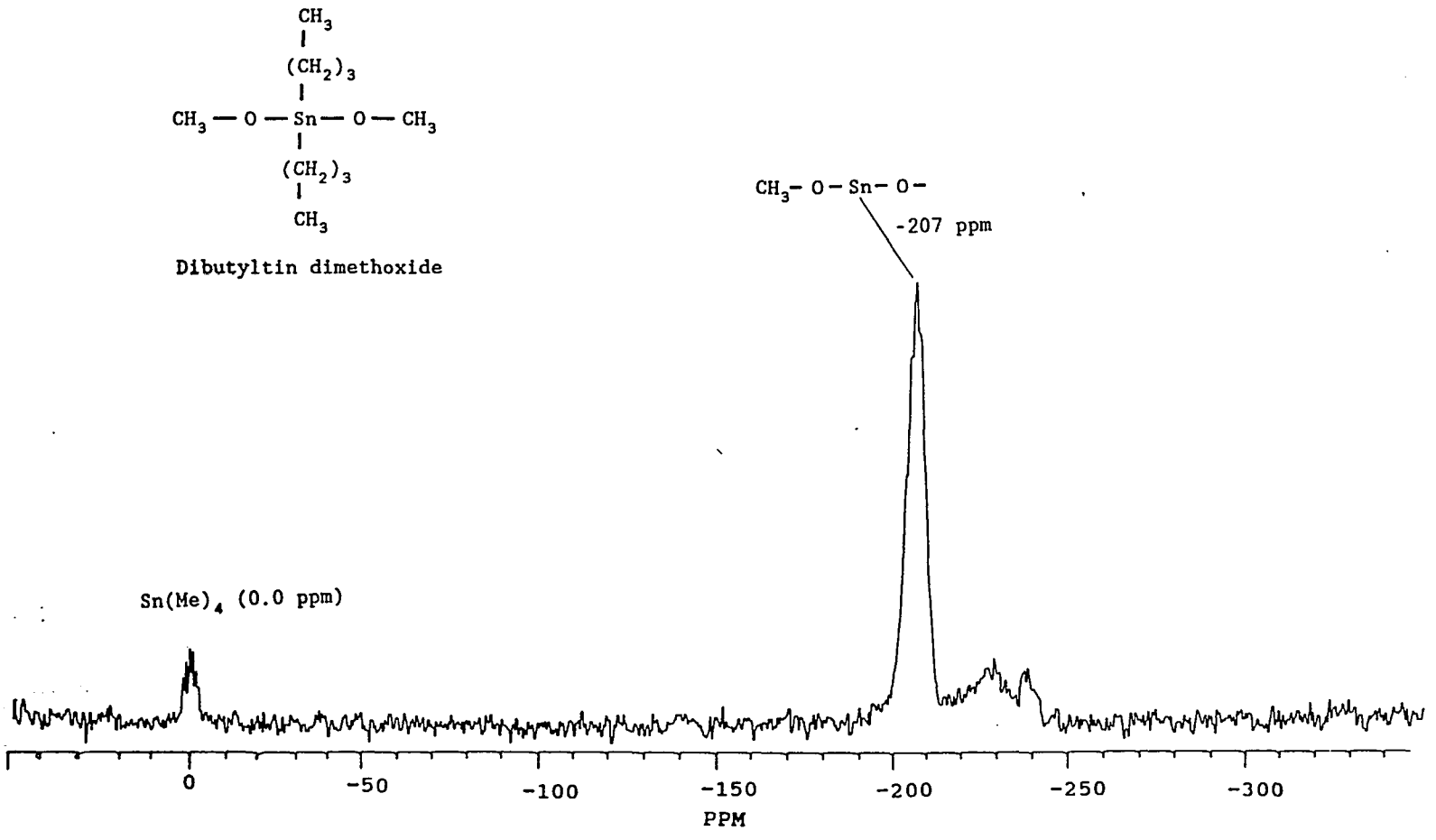


Fig. 2-24 ^{119}Sn NMR spectrum of dibutyltin dimethoxide in $CDCl_3$.

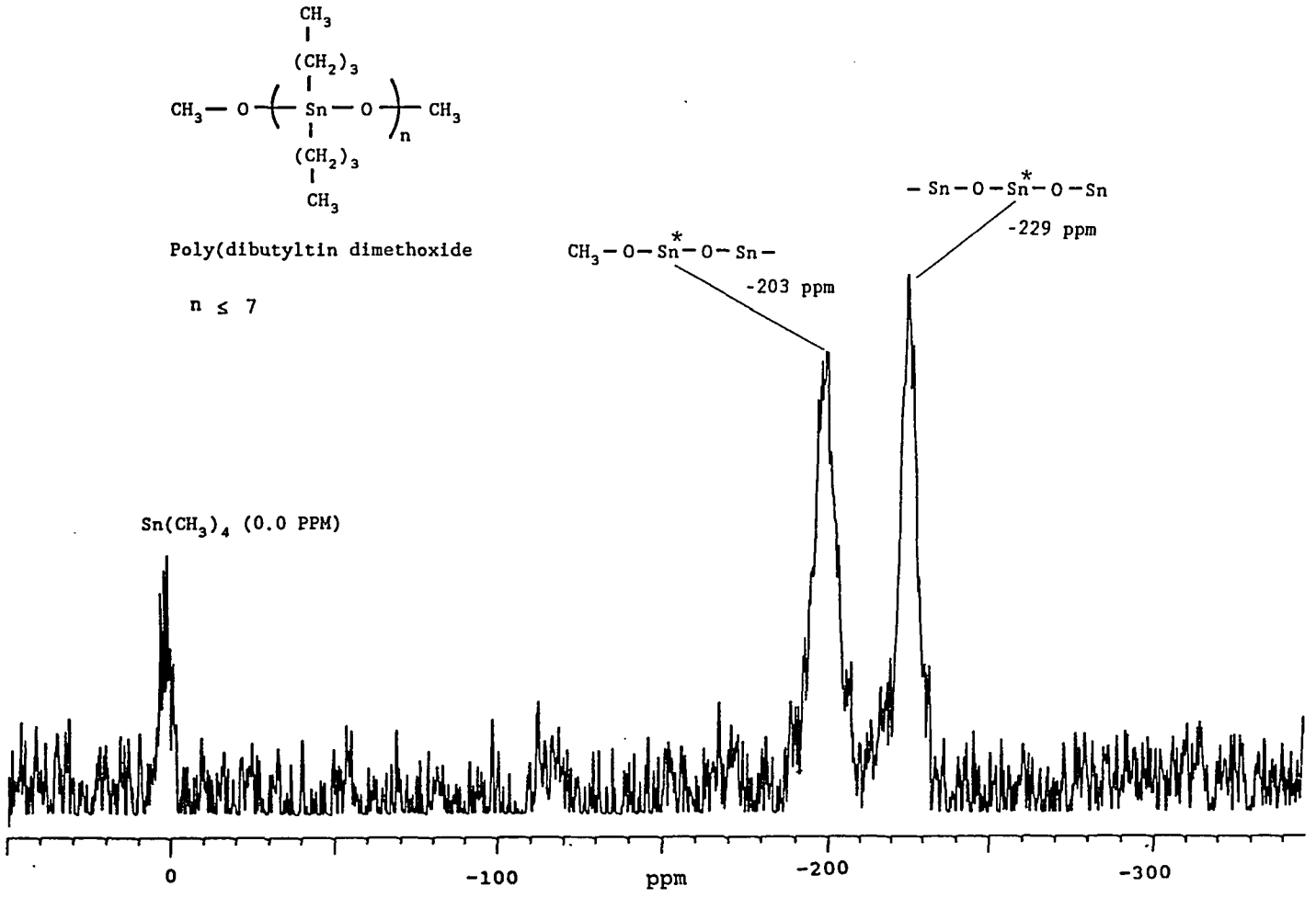


Fig. 2-25 ^{119}Sn NMR spectrum of poly(dibutyltinoxide) in $CDCl_3$.

2.3.4. Determination of Molecular Weight by ^{119}Sn NMR End Group Analysis and VPO Measurement

Based on two end groups per chain, the integrated areas of absorption M (Sn in main chains) and absorption E (Sn in end groups) in Fig. 2-7 can be used to estimate the molecular weight of the polymer using the following equation:

$$\overline{Mn} = \frac{\text{Area of main peak (M)}}{\text{Area of end group peak (E)}/2} X \quad \text{FW of repeat unit}$$

The peak areas were obtained using an integration software from New Methods Research Inc. The molecular weight of this polymer was estimated to be $\overline{Mn} = 1.2 \times 10^4$. The molecular weight obtained from VPO measurement is $\overline{Mn} = 1.0 \times 10^4$, a lower value than that determined by ^{119}Sn NMR analysis, most likely due to the presence of cyclic oligomers not accunted for in NMR analysis and other low molecular impurities.

2.3.5. Thermal Stability of Polymer

Figure 2-26 shows the TGA curves of this polymer; no weight loss (degradation) was observed at temperature lower than 220 °C. The weight loss curve show a two steps process. The mechanism for this behavior is not known at this time.

2.3.6. UV Spectroscopy and Photophysics

Figure 2-27 shows that the Polydibutylstannane

obtained has an absorption maximum at 371.5 nm in THF, approximately 38 nm, and 57 nm red shifted from its germanium [24] and silicon[26] counterpart with higher molecular weight respectively. As expected, the polydibutylstannane is highly light sensitive. Figure 2-28 shows the bleaching of a solution of this polymer in THF as a function of the UV irradiation time. The UV irradiation of this polymer leads to rapid photoscission. Photolysis also causes a rapid bleaching of the low energy absorption maxima, with λ_{max} shifting to shorter wavelengths and the absorptivity decreasing with irradiation. The bleaching is due to the formation of smaller polymer chains through scission processes, which decreases the extent of σ-conjugation along the polymer backbone, causing λ_{max} and absorbence to decrease. Similarly, this bleaching phenomenon have also been reported for organogermane[24] and organosilane polymers.[36] The rate of photoscission of polysilane (Fig. 2-29) was much lower than that of tin polymer under the same irradiation conditions. A decrease in absorptivity over 95 % was observed for the polystannane after irradiated by UV light for 4 seconds. However, only about 35 % decrease in absorptivity of polysilane was observed under same irradiation conditions. This clearly indicated that the organotin polymer is much more photosensitive than organosilicon polymers.

The absorption spectra of this polymer was also examined in solution as a function of temperature in order to answer the question of whether this polymer is

thermochromic like the related silicon and germanium polymers. Figure 2-30 shows the UV spectrum of thermochromic behavior of a solution of polydibutylstannane in THF. When the temperature was heated from 22 °C to 58 °C, absorption maximum was shifted from 371.5 nm to 366.9 nm. This thermochromic behavior is similar to polysilanes and polygermanes.[24] The reversibility of this process has not been established yet.

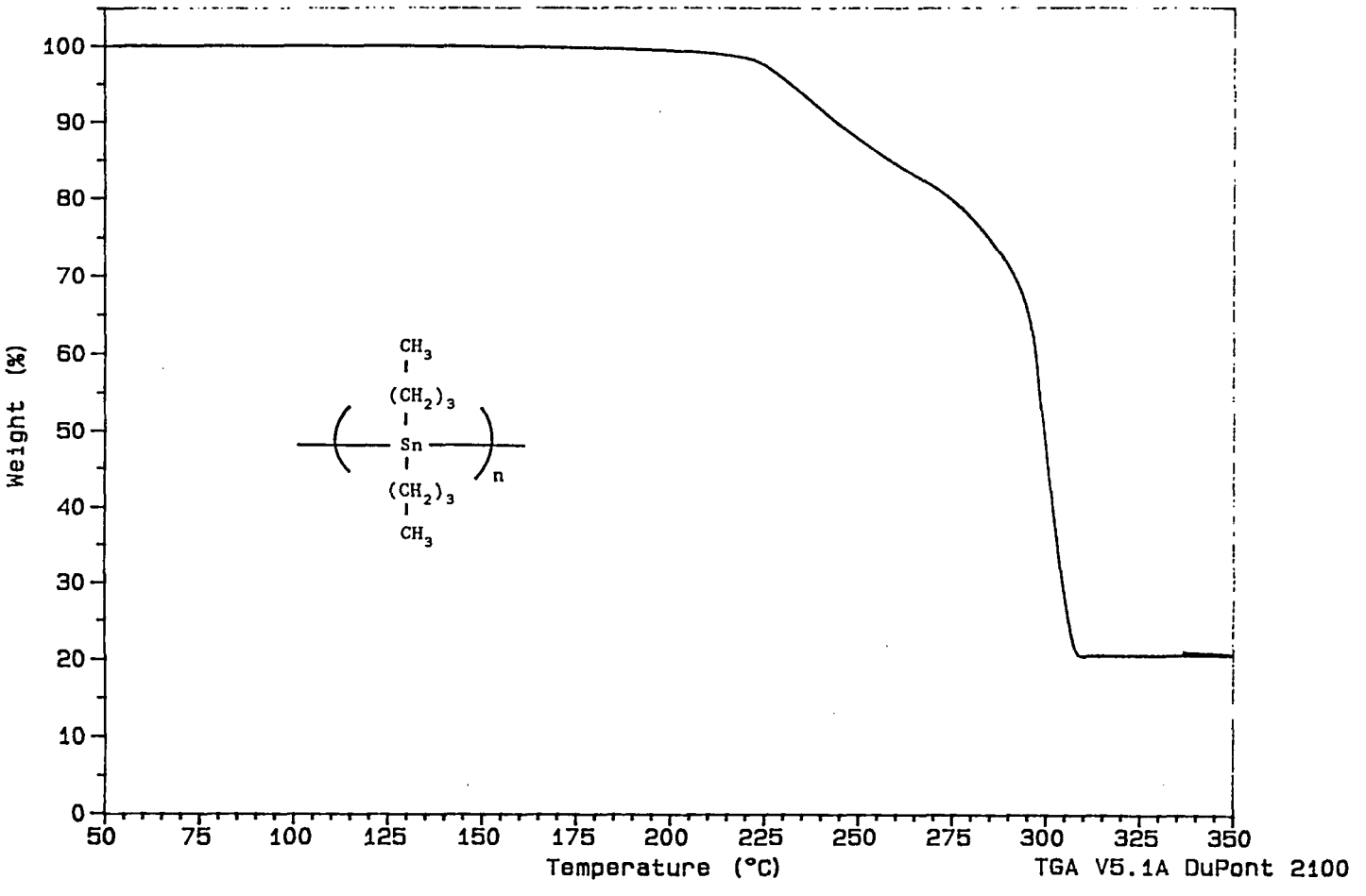


Fig. 2-26 TGA thermogram of polydibutylstannane.

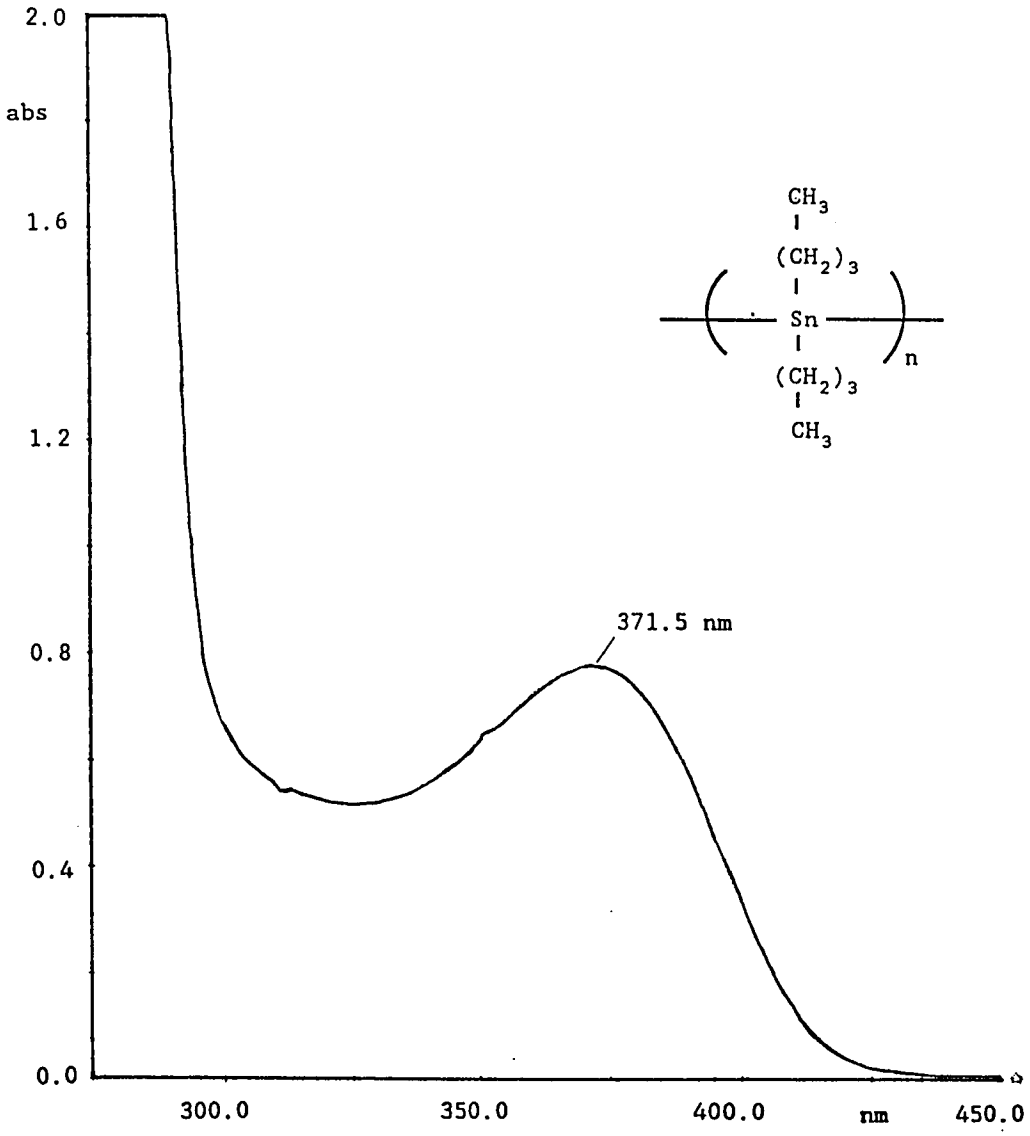


Fig. 2-27 UV spectrum of a solution of polydibutylstannane in THF (8.0×10^{-5} g/ml).

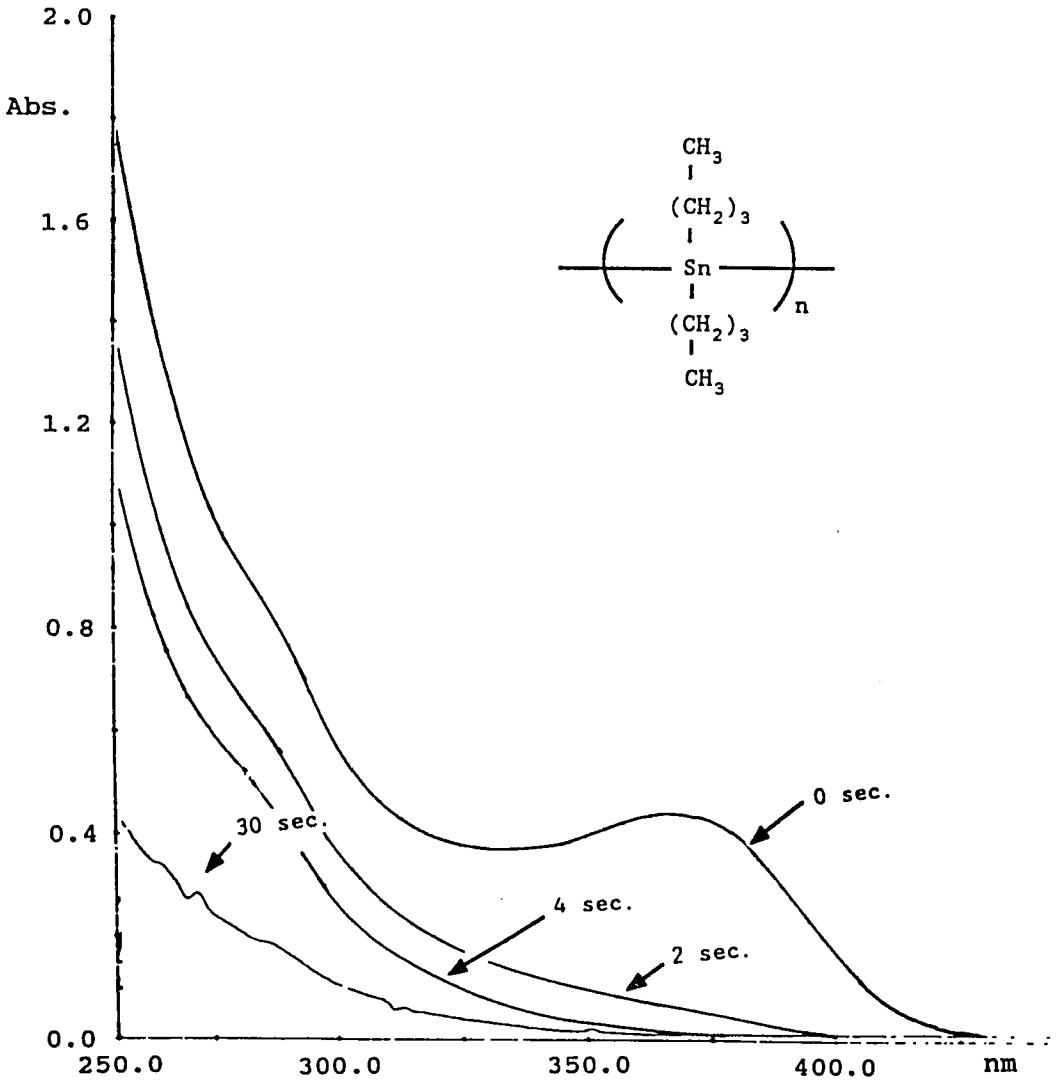


Fig. 2-28 Photochemical spectral bleaching of a solution of polydibutylstannane in THF upon UV irradiation time.

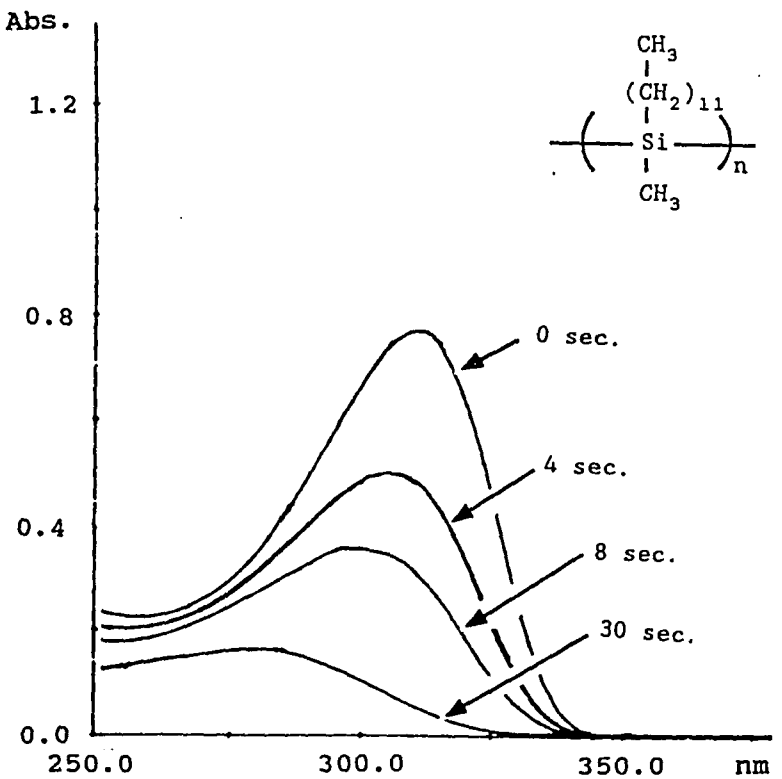


Fig. 2-29 Photochemical spectral bleaching of a solution of poly(n-dodecylmethylsilane) in THF upon UV irradiation time.

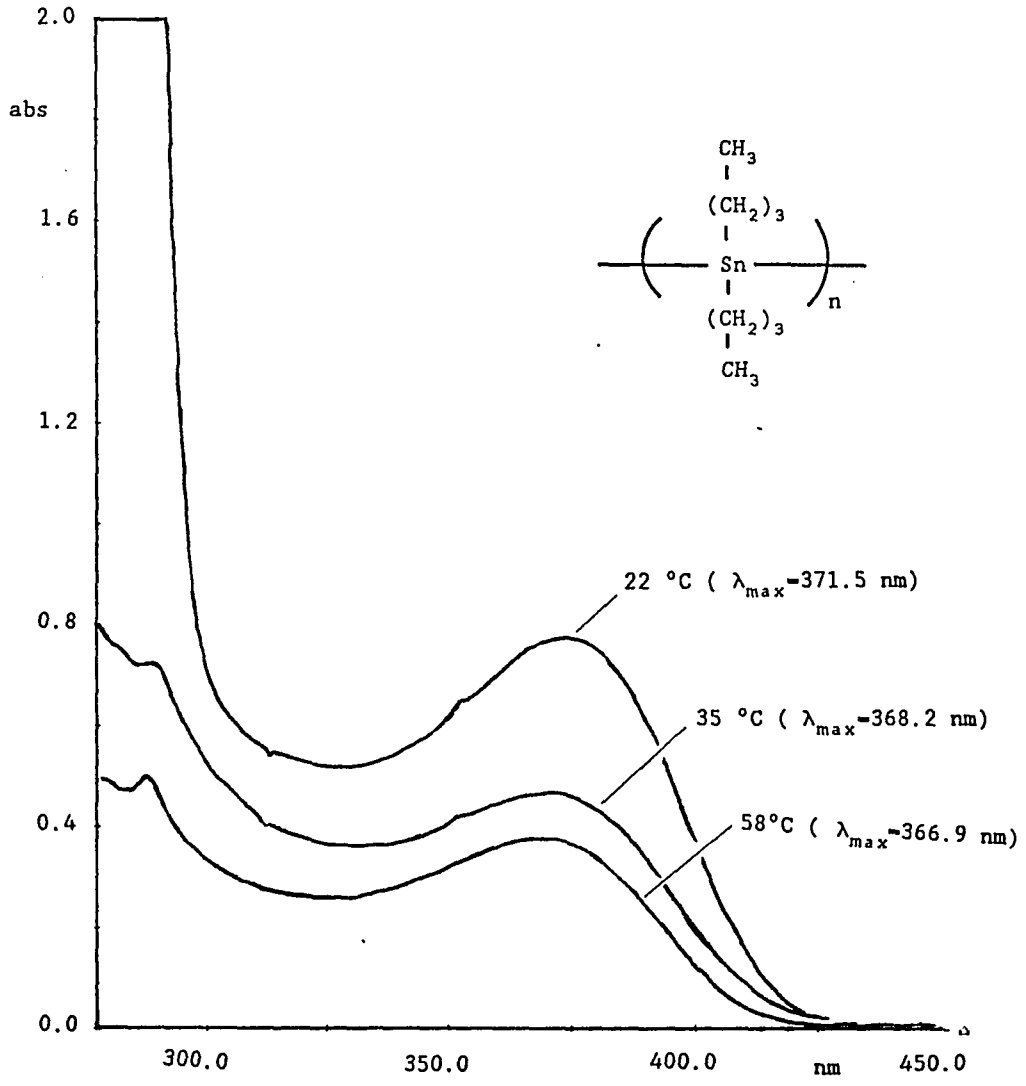
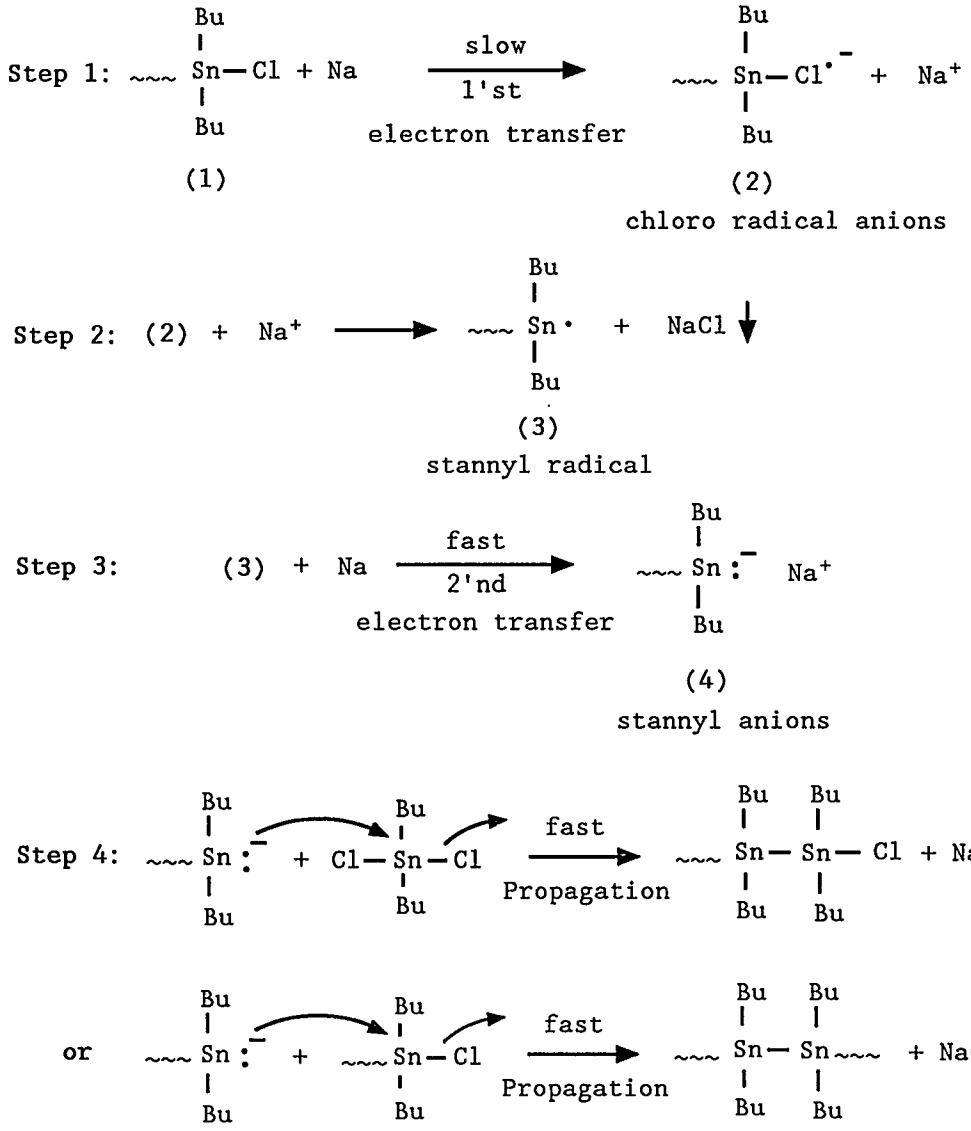


Fig. 2-30 Thermochromic behavior of a solution of polydibutylstannane in THF (8.0×10^{-5} g/ml).

2.5. Proposed Mechanism

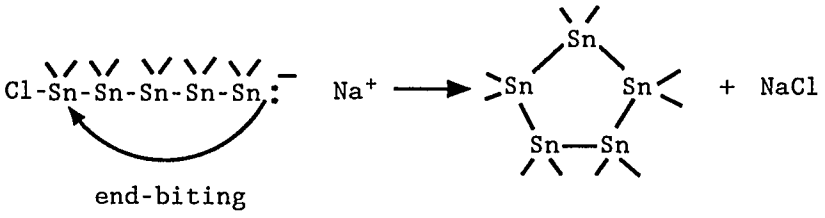
Based on an overview of the literatures of Wurtz coupling polymerizations of dichlorosilane[16,25-27], a reaction scheme for the formation of polydibutylstannane is proposed:



The first step in the polymerization is the electron transfer from sodium to dichlorotin, or terminal Cl of

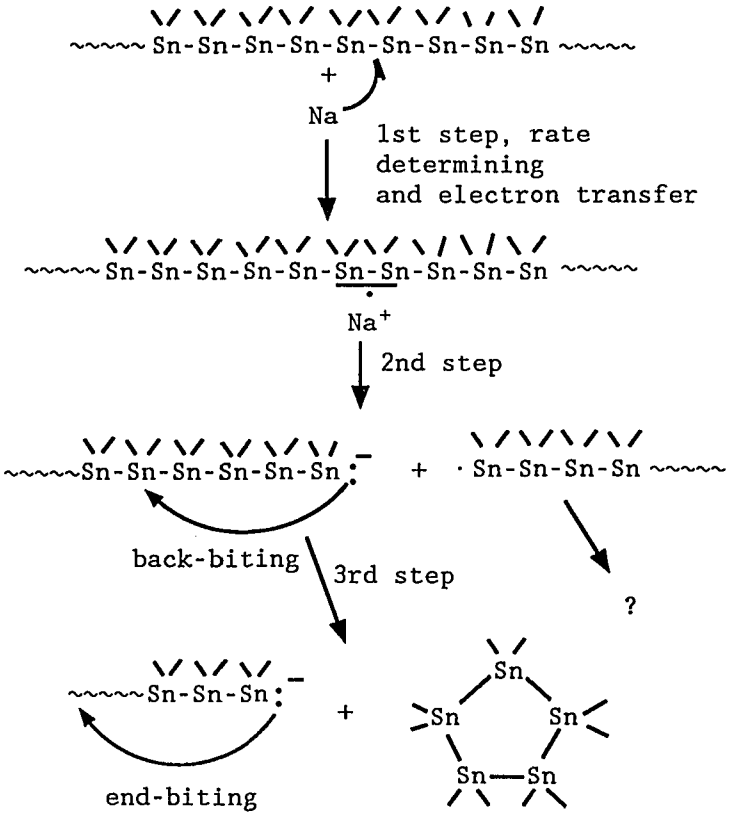
polymer chain to form a radical anions **(2)**. Upon elimination of the chloro anions, **(2)** is transformed to the stannyl radical**(3)**. This stannyl radical can be considered as an intermediate which rapidly participate in the second electron transfer, leading to the stannyl anions **(4)**. The stannyl anions reacts with monomeric dichlorides or displaces a terminal chloride to form a new Sn-Sn bond, i.e. a propagation step.

The molecular weight of the polystannane is still low compared with the polysilanes and the polygermanes. There are a few possible contributing factors for this phenomenon. First the reductive coupling proceeds by the reaction of stannyl anions with dichlorotin via a chain growth process. At the level of tetra-, penta-, or hexastannanes, the anionic center present at one end may react with its chloroterminated end instead of with a monomer.[27] This end-biting process will lead to the formation of cyclics:



Secondly, polystannane can be degraded more readily than carbon backbone polymers due to the relative weakness of Sn-Sn bond. In nonpolar solvents, the efficiency of the electron transfer is very slow or the reaction even does not occur at all. Therefore, for nonpolar conditions, the

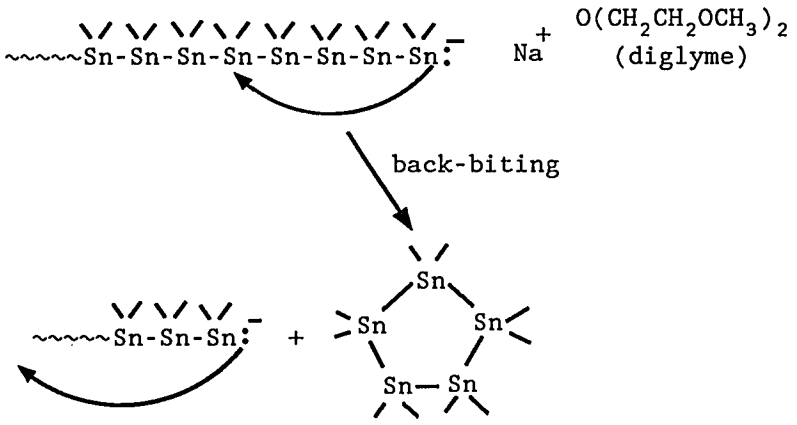
reaction require coordination additive such as crown ether or diglyme which can solvate alkali metal cations. Thus, the reactivity of the alkali metal is improved and the electron transfer process is accelerated. However, "too high" reactivity can lead to degradation of the polymer to cyclics. In the presence of crown ether, polystannane can be degraded by an excess of alkali metal to form cyclic oligomers as in the case for polysilane.[26] The rate of degradation depends on temperature, reaction time, solvent, alkali metal, amount of crown ether and amount of excess alkali metal. A suggested mechanism of the degradation is as follows:



It is possible that the first step, in which polymeric radical anion is formed, is the rate limiting step for degradation. It is facilitated, in the presence of crown ether or diglyme, due to solvation of a reaction product, Na^+ cations. The intermediate macromolecular radical anions can be cleaved to form a radical and an anion. The radical take a second electron to form the stannyl anion or it may recombine. The stannyl anions may also start cleaving Sn-Sn bonds by back-biting leading to the formation of cyclostannanes.

Still, another factor is that the crown ether or diglyme may increase the reactivity of stannyl anions by separating the counter ion, Na^+, from the anions center. This free macromolecular

anion is then in a better position for back-biting (degradation) process which leads to the formation of cyclic oligomers:



The present results clearly indicate that the back-biting (degradation) or end-biting is not important under the reaction condition at 60 °C: 5 mol% to 10 mol% of 15-crown-5 (based on amount of alkali metal used); sodium dispersions (2.05 times moles of monomer used); and a reaction time of less than 20 hours.

2.6. Conclusions

The first synthesis of high molecular weight polystannane has been accomplished through Wurtz-type coupling of dichlorotin. The synthetic expertise developed in this area will allow us to explore a broad spectrum of structural variations in this class of polymers.

Polymerizations at high reaction temperature (above 100 °C) does not occur without 15-crown-5. Polymerizations at high reaction temperature with 15-crown-5 causes rapidly degradation of polymer to cyclic oligomers.

Lower reaction temperatures favor high molecular weight; a preferable reaction temperature is at 60 °C.

Dibutyltin dichloride could only be polymerized in the presence of an additive (15-crown-5 or diglyme). This may be due to an increased solvation of the alkali metal cation which in turn leads to increased reactivity of the metal to accelerate electron transfer.

The UV spectra of polystannane show high absorptivity, ability to photodegrade, and bleaching behavior similar to polysilanes and polygermanes. The polymer differs significantly from the other polymers in its much higher light sensitivity.

This polymer was very sensitive to oxygen while in a solution due to oxygenation reaction.

It is thermally stable up to 220 °C, and soluble in chloroform, toluene, and THF.

The initial findings presented in this study clearly establish polystannanes as a new class of one-dimensional metallic chains with fundamental as well as technological significance.

Chapter III. Synthesis and Characterization of σ - Electron Conjugated Polymers and Their Nonlinear Optical Properties

3.1. Introduction

Third order nonlinearities in organic materials have attracted considerable interest recently owing to their potential applications in optical switching and optical computing devices.[1,2] Organic materials offer many advantages over the inorganic materials developed to date, including large nonlinearities with fast response times and easy of processing. However, π-conjugated carbon-based polymers, which so far have proved to be the most promising candidates for third order nonlinear materials, often suffer from the disadvantages of having large absorption bands in the visible or near-infrared regions of the spectrum and chemical instability.

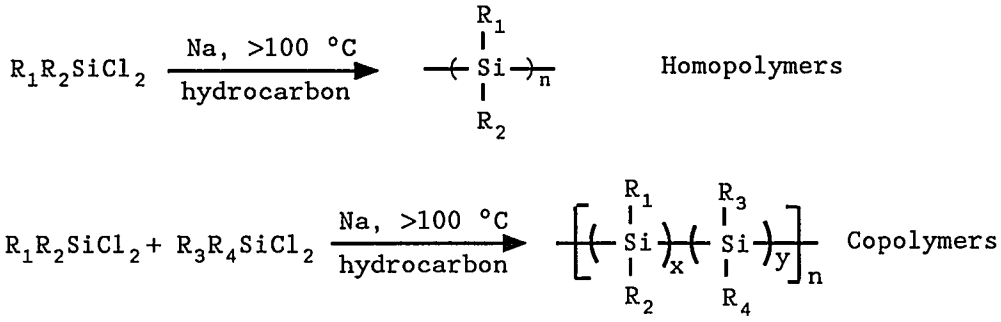
The polysilane polymers represent another distinct class of conjugated polymers which are remarkably different from π-conjugated carbon-based polymers. These polymers have a molecular structure: $\leftarrow SiR_1R_2\rightarrow_n$, i.e., a long catenated σ bonded silicon backbone with two side groups R_1 and R_2 attached to each silicon atom. They are thermally and oxidatively stable, soluble in most hydrocarbon solvents and offer physical, chemical, and optical properties that render them suitable for various applications in optics. Polysilanes have been developed as photoresists for

electron-beam lithography[3] and ultraviolet photolithography.[4-6] Exploitation of the birefringence produced following two-photon absorption of visible light[7,8] allows for the fabrication of optical device structures such as channel waveguides and gratings.[9,10]

In spite of the σ bonded nature of the backbone, the polysilanes show extensive electronic delocalization, resulting in strong transitions for excitations polarized parallel to the backbone. They are unique in that the electron delocalization along the backbone chromophore makes the polymer transparent throughout the visible and near-infrared regions but exhibit large absorption bands in the 250-400 nm region, depending on the substituents, Si repeat length, crystallinity, and orientation. Previously, some substituted polysilanes were shown to have third order nonlinear susceptibility $\chi^{(3)}$ in the range $10^{-12} \sim 10^{-11}$ esu.[11-14] Although these values are not as large as those of other π-conjugated carbone-based polymers, e.g., polydiacetylenes.[15] The effects of substituents groups and orientation effects in polysilanes on the nonlinear optical properties have not yet been fully investigated. Further increases in $\chi^{(3)}$ may be possible through appropriate selection of side groups. The major advantage of a broad range of optical transparency makes further investigation of these materials highly desirable.

Polysilane polymers are usually made by the reaction of organodichlorosilanes with sodium metal in an inert hydrocarbon diluent at temperatures above 100 °C.[16] Both

very high molecular weight (100,000-2,500,000) homopolymers[16] and copolymers[17] can be synthesized as follows:



The groups R_1-R_4 include a wide variety of aryl and alkyl groups. The number of possible polysilane polymers is very large. One of the more interesting features of these materials is their unusual electronic spectra.[18] The UV absorption maxima λ_{max} in polysilanes at room temperature strongly depend on the nature of the substituents attached to the backbone. The absorption maxima λ_{max} of alkyl substituted polysilanes move to longer wavelength from about 305 nm for small alkyl substituents ($(MeMeSi)_n$) to 322 nm in large alkyl substituents ($(cyclo\text{-}C_6H_{11}SiMe)_n$). Since the electronic interaction of Si with different alkyl substituents should be similar, the difference in the absorption spectra are thought to result from conformational changes in the polymer chain with increasing alkyl group size, which alters the orbital energies.[19] Orbital models predict a bathochromic shift of λ_{max} should occur with increasing trans population in the polymer backbone.[20,21]

Aryl substituents interact electronically with silane backbone to lower the transition energy. A significant spectral changes occur when aromatic groups are directly bonded to the backbone. In these cases, the bathochromic shift of 20-30 nm observed has been attributed to mixing of the σ and σ^* orbitals of the backbone with the π and π^* orbitals of the aromatic substituents.[18,19] The UV excitation energy may also be reduced by mixing of the σ^* like, excited state orbitals with aryl π^*.[22]

Four polysilanes with different substituents: Poly(phenylmethylsilane), poly(phenylmethyl-co-diphenylsilane), poly(cyclohexylmethylsilane) and poly(n-dodecylmethylsilane) were synthesized in this work. The third order nonlinear susceptibility $\chi^{(3)}$ and the ultrafast time response of optical nonlinearity of poly(phenylmethylsilane) thin films and solutions were measured using both picosecond Optical-Kerr Gate (OKG)[13] and Degenerate Four Wave Mixing (DFWM)[23-25]. The sign of χ^3 in poly(phenylmethylsilane) was determined using the single beam Z-scan technique[26,27] with picosecond pulses at both 532nm and 1064 nm.[28] The sign is an important parameter for many nonlinear optical applications, such as self-focusing. The near infrared third order optical nonlinearity of above four polysilanes in solutions and films were also measured using degenerate four wave mixing (DFWM) with picosecond pulse at 1064 nm. These four polysilanes can be divided into two classes: the first two polysilanes have side groups with π-electrons in aryl substituents and σ-electrons

in backbones; and the last two polysilanes have only σ-electrons in backbones. The effects on the nonlinear optical properties excerted by the different side groups has been also studied.

The first synthesis of polysilane with pyridyl functional group is also reported in this chapter. Today, most of the substituents groups of polysilanes have been limited to organic radicals such as aryl, alkyl, and trimethylsilyl groups etc. Polysilanes with functional side groups have not been explored to any significant extent. Although they might have very interesting properties. For example, solubility of polymers could be varied in a controlled way. The physical, spectral, chemical, conductive and nonlinear optical properties of polysilanes can also be controlled. Some substituents may increase stability of intermediate silylenes and facilitate photodegradation. Others may increase photostability of polymers. We have been interested in polysilanes with pyridinyl functional groups, because their synthesis may lead to broader scope of possibilities.

There have been no reports on the synthesis of this polymer. This polymer resembles stucturally poly(phenylmethylsilane). However, the presence of nitrogen atom in the pyridine ring may imparts new basic properties to the polymer and dramatically alters its physical and chemical characteristics. The weakly basic nitrogen atom makes possible a variety of reactions on pyridyl-containing polysilanes, e.g. reaction with acids, quaternization, and

complexation of metals.

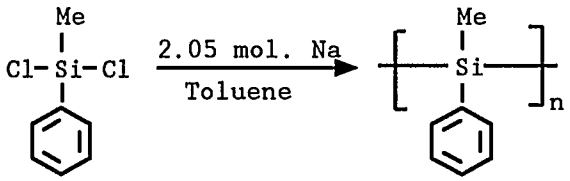
3.2 Experimental

All dichlorosilane monomers were purchased from Huls. They were carefully fractionally distilled immediately prior to use. All solvents were dried in CaH_2 and distilled and then stored under N_2 atmosphere. Sodium spheres in toluene was purchased from Aldrich. All reactions are very sensitive to moisture. Complete removal of moisture from the reaction system was necessary to obtain pure products. Operations were conducted using syringe techniques. The entire apparatus was assembled and flamed to remove residual moisture from the system. All reactions have been carried out under dry nitrogen atmosphere.

The nonlinear optical properties of polysilanes have been also studied. Measurements of the nonlinear optical properties by laser experiments were performed by Dr. Lina Yang at the Institute for Ultrafast Spectroscopy and Laser and Photonic Application Laboratory, The City College of The City University of New York.

3.2.1. Synthesis of Poly(phenylmethylsilane)

Poly(phenylmethylsilane) was prepared via the following scheme:[16]

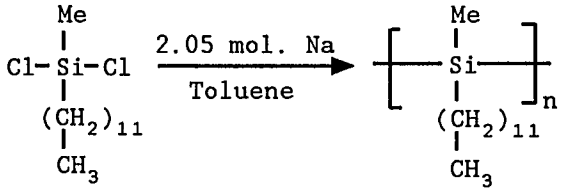


phenylmethyldichlorosilane (25 g, 0.131 mol) was dissolved in 100 ml of dry toluene and 6.2 g (0.27 mol) of sodium spheres was added in an "inverse addition" manner to a refluxing toluene/monomer mixture at a slow rate under moderate stirring and the protection against ambient light. Three hours after the addition of sodium spheres, the polymer was obtained by precipitation from the toluene solution with isopropyl alcohol (10:1, ratio of isopropyl alcohol to solution by volume), followed by dissolution in 20 ml of toluene and washed with 200 ml of distilled water. The organic layer was separated and washed with 200 ml of distilled water to remove traces of sodium salts. The polymer was purified by reprecipitation from the solution with isopropyl alcohol (10:1 ratio of isopropyl alcohol to solution by volume). Finally, 6.5 g (yield 41.3 %) of poly(phenylmethylsilane) were obtained.

3.2.2. Synthesis of Poly(n-dodecylmethylsilane)

Poly(n-dodecylmethylsilane) was prepared via the

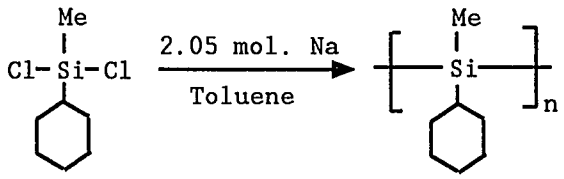
following scheme:



The procedure of synthesis of poly(phenylmethylsilane) was repeated using as reactants 25 g .(0.088 mol) of n-dodecylmethyl dichlorosilane and 4.2 g (0.183 mol) of sodium spheres in 100 ml of dry toluene. A yield of 38.6 % (7.4 g) of polymer was obtained.

3.2.3. Synthesis of Poly(cyclohexylmethylsilane)

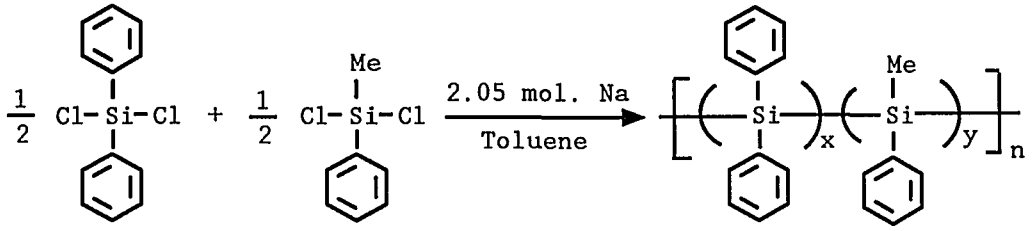
Poly(cyclohexylmethylsilane) was prepared via the following scheme



The procedure of synthesis of poly(phenylmethylsilane) was repeated using as reactants 25 g (0.129 mol)of cyclohexylmethyl dichlorosilane and 6.0 g (0.261 mol) of sodium spheres in 100 ml of dry toluene. A yield of 41.0 % (6.5 g) of polymer was obtained.

3.2.4. Synthesis of Poly(phenylmethylsilane-co-diphenylsilane)

Another opolymer containing diphenyl silylene units together with another units, MePhSi, was prepared as follows:[17]



Sodium dispersion (2.42 g, 0.105 mol) and 35 ml of toluene were added to the reaction flask and the stirred mixture was heated to gentle reflux. A mixture of diphenyldichlorosilane (6.32 g, 0.025 mol) and phenylmethyldichlorosilane (4.77 g, 0.025 mol) was added dropwise at a rate of maintaining vigorous refluxing. After the addition was complete, the mixture was refluxed for additional 2 hours. The reaction mixture was cooled to room temperature and quenched with 13 ml of ethanol and 125 ml of water. The organic layer was separated and washed with 125 ml water to remove traces of salts. Toluene was then stripped off using a rotary evaporator, and the greasy residue was dissolved in 20 ml of THF. A mixture of 200 ml of methanol and 100 ml of 2-propanol was slowly added to the THF solvent under stirring to precipitate the copolymer. To remove traces of solvents and any volatile by products, the precipitate was dried a vacuum oven (2 mm Hg) at 80 ^{0}C. A yield of 46 % (2.5 g) of polymer was obtained.

3.2.5. Preparation of Optical Clear Films of Poly(phenylmethylsilane) for Nonlinear Optical Properties Study

High optical transparency, uniform thickness films of poly(phenylmethylsilane) was prepared in a large crystallization dish with controlled vapor pressure of THF solvent. One g of poly(phenylmethylsilane) were dissolved in 6.0 ml of toluene and filtered though a 0.5 μm filter. This system of large crystallization dish with controlled vapor pressure of the THF solvent was first allowed to reach equilibrium, i.e., vapor saturation. The solution was then introduced to glass slides with minimum exposure to ambient atmosphere and solidification took place in about one hour. Film samples were allowed to evaporate further at ambient conditions then sealed for laser experiment. These films were transparent, optically clear, and uniform.

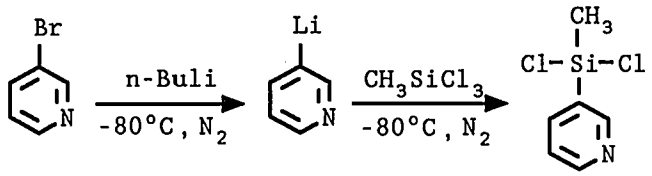
3.2.6. Preparation of Polysilanes Solutions for Nonlinear Optical Properties Studies

Poly(phenylmethylsilane), poly(n-dodecylmethylsilane), poly(cyclohexylmethylsilane), and poly(phenylmethylsilane-co-diphenylsilane) were dissolved in tetrahydrofuran (THF) separately in required concentration and purified by filtration though a 0.5 μm filter.

3.2.7. Synthesis of 3-bromopyridinedichlorosilane Monomer

The method of preparation monomer was essentially that of M. Zeldin.[29] The synthetic reaction can be depicted as

follows:

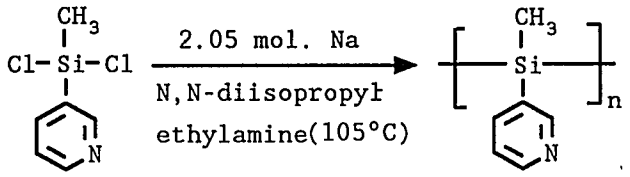


The reaction was very sensitive to moisture. Complete removal of moisture from the reaction system was critical to obtain pure product.

3-Bromopyridine (26.22 g, 0.166 mole) in 50 ml of dry ether was added under dry nitrogen at -80 °C dropwise to a well stirred dry ether (100 ml) solution of n-butyllithium (2.5 M in hexane, 67 ml) in a 500 ml round bottom flask. The mixture was stirred for 2 hours. The yellow suspension was transferred under dry nitrogen to a jacketed dropping funnel cooled with dry ice/acetone. The suspension was added dropwise to excess trichloromethylsilane (1.29 mole) at -80 °C under dry nitrogen. The mixture was stirred for 2 hours and allowed to warm to room temperature. The resulting salt was filtered under dry nitrogen and volatile solvents and unreacted CH_3SiCl_3 were removed under vacuum. The residual material was distilled to give a colorless 3-pyridylmethyldichlorosilane with a Yield of 35% (11.16g).

3.2.8. Polymerization of 3-pyridylmethyldichlorosilane

The synthetic reaction can be depicted as follows:



Polysilanes are usually made by the reaction of organodichlorosilanes with sodium metal in an inert hydrocarbon diluent at temperature above 100 °C.[16] But the polymerization of 3-pyridyl-methyldichlorosilane was unsuccessful through the use of hydrocarbon diluent as solvent.

3-Pyridylmethyldichlorosilane (3.67 g) was dissolved in 10 ml of n,n-diisopropylethylamine (dried by refluxing 14 hours over sodium metal) and 0.94 g of sodium spheres were added to the reaction flask and the stirred mixture was heated to 105 °C and allowed to react for 18 hours. All reaction operations were carried out under dry nitrogen. The resulting salt was removed by filtration. The product was obtained by precipitation from the filtrate with water (10:1, ratio of water to filtrate by volume) and washed further with water two times to remove traces of salt. The remainder of the product consists of low molecular weight including cyclic oligomers and a large of amount (19.2 %) of insoluble materials. The polymer was purified by reprecipitation from the DMF solution with ether (Yield: 20.5 %). This polymer is soluble in THF, methanol, DMF and DMSO.

3.2.9. NMR Characterization of Polysilanes

All NMR spectra were obtained with a IBM WP-200 SY Fourier Transform NMR Spectrometer operated at 200 MHz for proton using Bruker software. The chemical shifts were referenced to tetramethylsilane at 0 ppm for ^{1}H and ^{29}Si spectra and $CDCl_3$ at 77 ppm for ^{13}C spectra.

3.2.10. UV Spectroscopy of Polysilanes

The UV spectra were obtained on a Varian DMS 300 UV Visible Spectrophotometer.

3.2.11. Determination of Molecular Weight of Poly(3-pyridylmethylsilane)

The molecular weight of poly(3-pyridylmethylsilane) was determined by VPO measurements with an UIC 070 VPO Semi-automatic Vapor Pressure Osmometer at 50 °C with benzil as calibration standards and THF as solvent.

3.2.12. Thermal Stability of Poly(3-pyridylmethylsilane)

The thermal stability of poly(3-pyridylmethylsilane) was determined by TGA techniques with a DuPont Thermal Analyzer, Model 990. The sample size of polymer was 5 mg. The heating rate was 10 °C/min. from 50 °c to 300 °C under the atmosphere of nitrogen.

3.2.13. Nonlinear Optical Properties of Polysilanes

The main laser source used in the experiments was the commercially available 30 picosecond (ps) Quantel Nd:YAG

laser (YAG denotes yttrium-aluminum-garnet), which is both passively and actively mode locked.

(i). Third order Nonlinear Susceptibility $\chi^{(3)}$ and Ultrafast Time Response of Optical Nonlinearity in Poly(phenylmethylsilane)

The third order nonlinear susceptibility $\chi^{(3)}$ and the response time of nonlinear optical process of poly(phenylmethylsilane) in thin films and solutions were measured using both the picosecond (OKG)[13] and DFWM)[23]. The samples of thin films and solutions used here were prepared by the methods described in the sections 3.2.5 and 3.2.6 respectively. The single optical pulses with ~8ps (full width at half maximum) duration were generated from a mode-locked Nd:glass laser with a single-pulse selector, an amplifier and a second harmonic generator. The pump and probe wavelengths were at 1060 nm and 530 nm, respectively. Further details of these experimental techniques were described in reference 13 and 24.

(ii). Signs of $\chi^{(3)}$ in Poly(phenylmethylsilane)

The signs of $\chi^{(3)}$ in poly(phenylmethylsilane) were determined using the single beam Z-scan technique[27,28] with a mode-locked Quantel YAG Laser with a frequency doubler provided laser pulses with a 30 ps duration at 532 and 1064 nm at a 10 Hz repetition rate. The sample used here was a solution (0.5 M) in the tetrahydrofuran (THF) solvent. The poly(phenylmethylsilane) solution was contained in a 1 mm

cuvette. A 1 mm diameter aperture was placed at a distance of more than 1.5 m away from the focus point. The light transmission through the aperture was detected, recorded, and analyzed by a photomultiplier (PMT) and a boxcar average interfaced with a microcomputer. Each data point was an average over 30 shorts. Narrow Band Filters (either NB532 or NB1064) were used in front of the PMT. Z-scans from a 1 mm cell containing CS_2 or THF solvents were also measured and used as standards and references.

(iii). Near Infrared Optical Response in Polysilanes

The near infrared third order optical nonlinearity has been studied using DFWM [23] with picosecond pulse at 1064 nm. Poly(phenylmethylsilane), poly(phenylmethylsilane-co-diphenyl silane), poly(cyclohexylmethylsilane) and poly(n-dodecylmethylsialne) have been chosen for study in this work. The thin film and solution samples used here were prepared by the methods described in sections 3.2.5 and 3.2.6 respectively.

3.3. Results and Discussion

3.3.1. Determination of Structures of Polysilanes by ^1H, ^{13}C, and ^{29}Si NMR Spectra

The structures of these polymers were determined by ^1H, ^{13}C and ^{29}Si NMR spectra. Figure 3-1 shows a ^1H NMR spectrum of poly(phenylmethylsilane). A broad absorption in the region 0.3 ppm to -1.1 ppm was due to the protons of

methyl group. A broad absorption in the region 6.2 ppm to 7.45 ppm was due to the protons of benzene ring. The ratio of integrated absorptions of protons in benzene ring /methyl, 1.72/1, is very close to the required value of 1.67/1. The experimental value was slightly larger than the theoretical value due to the absorption of $CDCl_3$ overlapping with that of benzene ring. Figures 3-2 shows a ^{13}C NMR spectrum of this polymer with assignments of absorptions. A singlet at -18.5 ppm due to silicon in the backbone was observed in the ^{29}Si NMR spectrum (Fig. 3-3).

Figure 3-4 shows a ^{1}H NMR spectrum of poly(n-dodecylmethylsilane). A absorption at 0.2 ppm was assigned to the methyl group bonded with silicon. A multiplet at 0.8 ppm was assigned to methylene group bonded with silicon and methyl group in n-dodecyl side chain. As shown in the Figure 3-4, the experimental value of the ratio of the integrated absorptions matches the theoretical value. Figures 3-5 and 3-6 show the ^{13}C and ^{29}Si NMR spectra respectively.

Figures 3-7 and 3-8 show the ^{1}H and the ^{13}C NMR spectra of poly(cyclohexylmethylsilane) and their assignments.

Figures 3-9 and 3-10 show the ^{1}H and the ^{13}C NMR spectra of poly(phenylmethylsilane-co-diphenylsilane).

^{1}H and ^{13}C NMR spectra of 3-pyridylmethyldichlorosilane monomer with their assignments are shown in Figures 3-11 and 3-12. The ratio of integrated absorptions of protons in pyridine ring to methyl matches the required value of 1.3/1. The ^{1}H and ^{13}C NMR spectra of this polymer are shown in

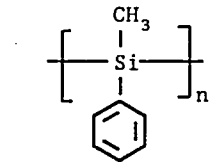
Figures 3-13 and 3-14.

3.3.2. UV Spectroscopies of Polysilanes

Delocalization of σ-electrons in polysilanes is apparent from their UV absorption spectra. The UV spectra of alkyl substituted polysilanes such as poly(n-dodecylmethylsilane) and poly(cyclohexylmethylsilane) show strong electronic absorption maximum at 310.1 nm (Fig. 3-15) and 322.0 nm (Fig. 3-16) respectively. The electronic transition has been assigned to be from a ground state consisting of delocalized σ_{Si-Si} bonding orbitals[30-32] to an excited state consisting primarily of σ^*_{Si-Si} and σ^*_{Si-C} components, with apparently minimal involvement of 3 *d* orbitals[33,34]. The UV spectra absorption of poly(phenylmethylsilane) (Fig. 3-17, λ_{max}= 337.0 nm) and poly(phenylmethylsilane-co-diphenylsilane) (Fig. 3-18, λ_{max}= 348.9 nm) exhibit a significant spectral changes when the aromatic group is directly bonded to the backbone. Both the wavelength and the molar absorptivity of the lowest-energy UV band for these polymers increased with increase in the proportion of phenyl substituents[35,36]. The poly(phenylmethylsilane) containing one phenyl side group per backbone repeat unit absorbs at 337.0 nm. The copolysilane containing more than one phenyl side groups per backbone repeat unit absorbs at 348.9 nm. The bathochromic shift of 27 nm and 38 nm observed in poly(phenylmethylsilane) and poly(phenylmethylsilane-co-diphenylsilane) compared with poly(n-dodecylmethyl- silane) respectively

have been attributed to mixing of the σ and σ^* orbitals of the backbone with the π and π^* orbitals of the aromatic substituents.[18,37]

$$\text{Theoretical value} = \frac{\text{number of protons in benzen ring}}{\text{number of protons in } CH_3} = \frac{5}{3} = 1.67$$



Poly(phenylmethylsilane)

$$\text{Experimental value} = \frac{\text{area of } \bigcirc \text{ peaks}}{\text{area of } CH_3 \text{ peaks}} = \frac{201.7}{117.4} = 1.72$$

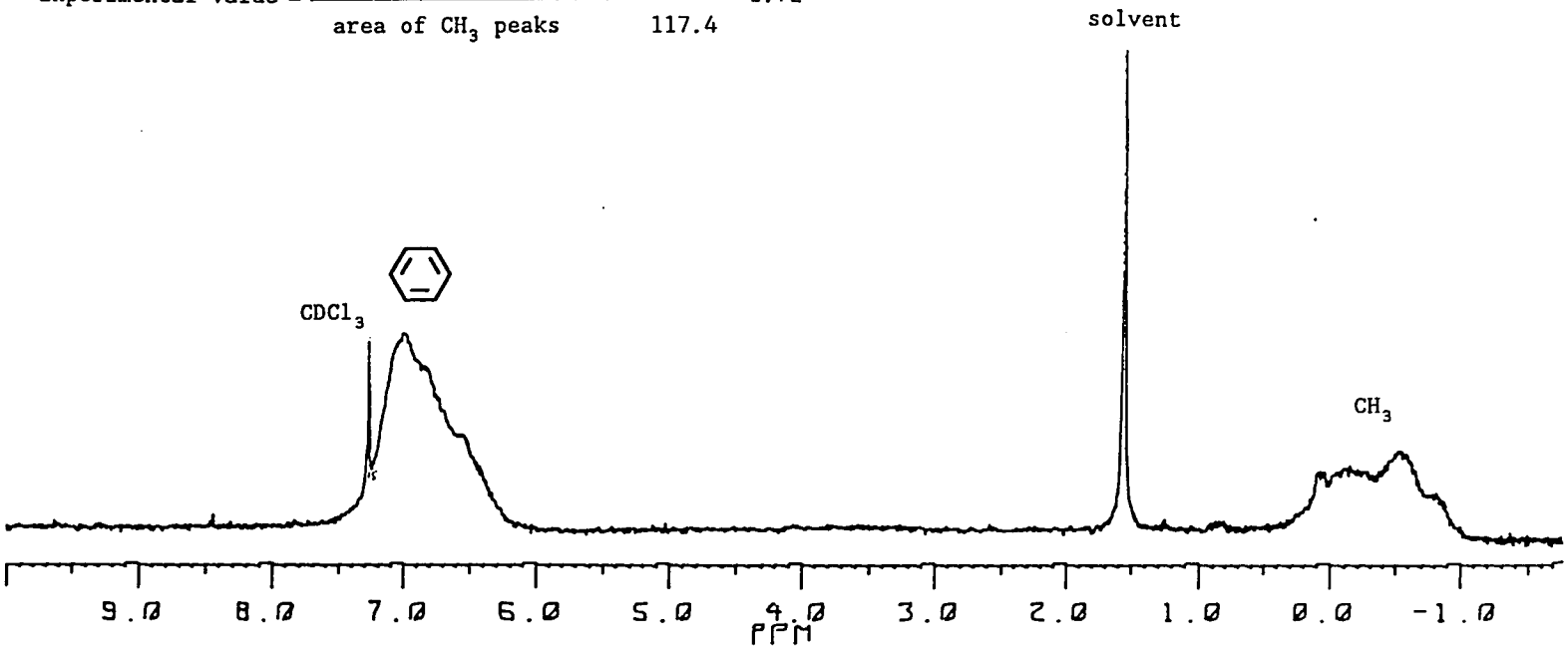


Fig. 3-1 ^{1}H NMR spectrum of poly(phenylmethylsilane) in $CDCl_3$

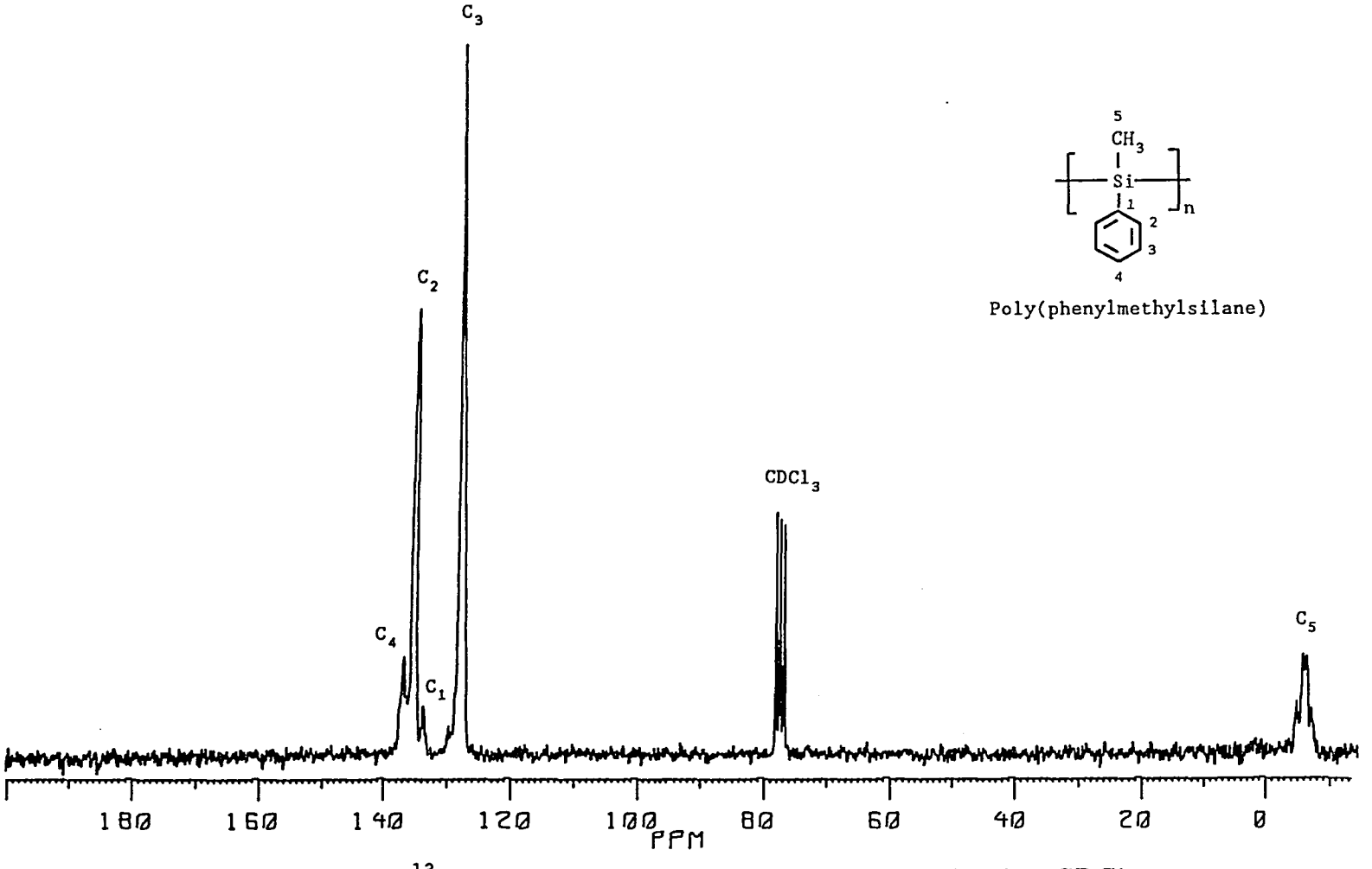


Fig. 3-2 ^{13}C NMR spectrum of poly(phenylmethylsilane) in $CDCl_3$

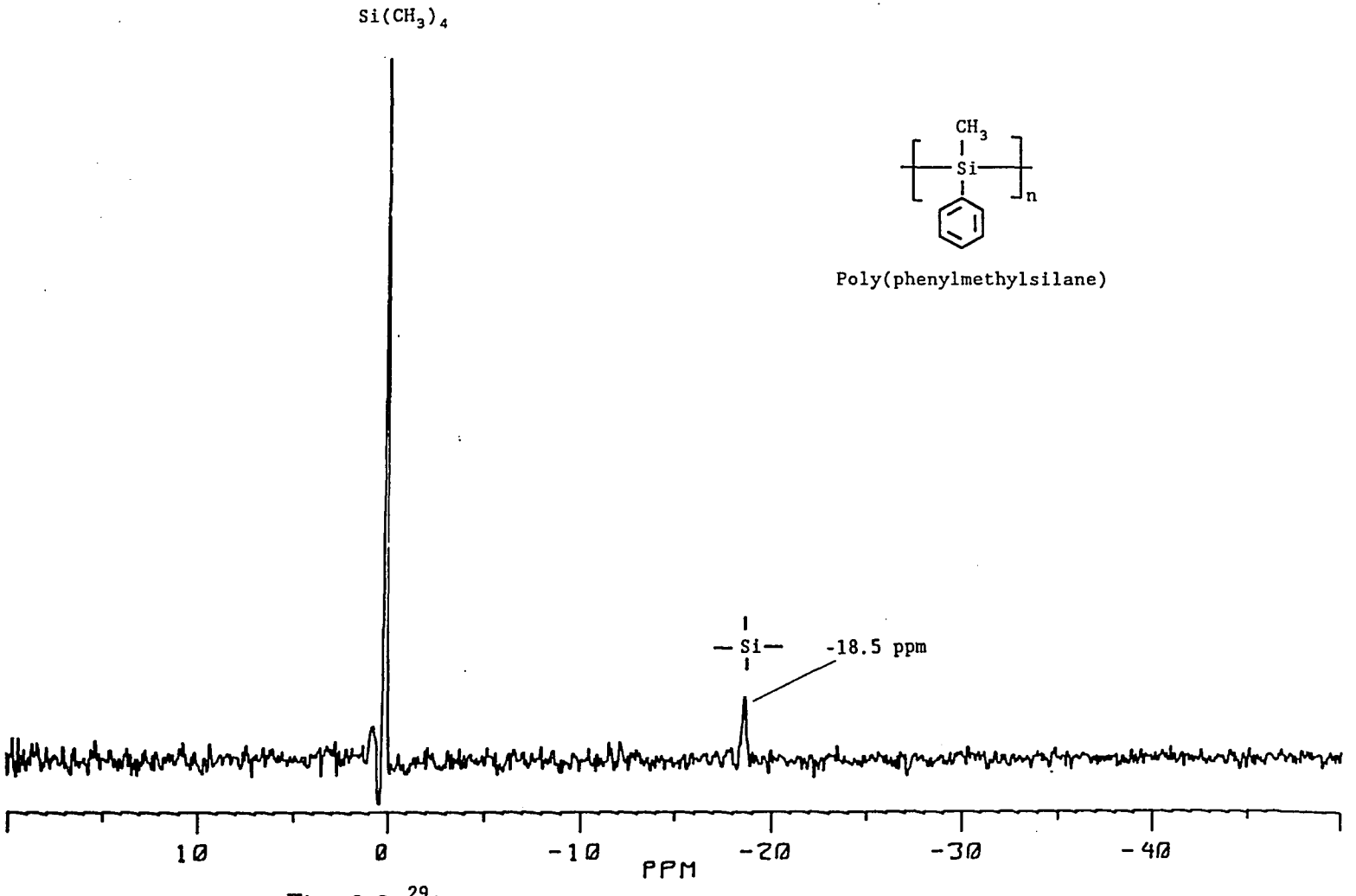


Fig. 3-3 ^{29}Si spectrum of poly(phenylmethylsilane) in $CDCl_3$

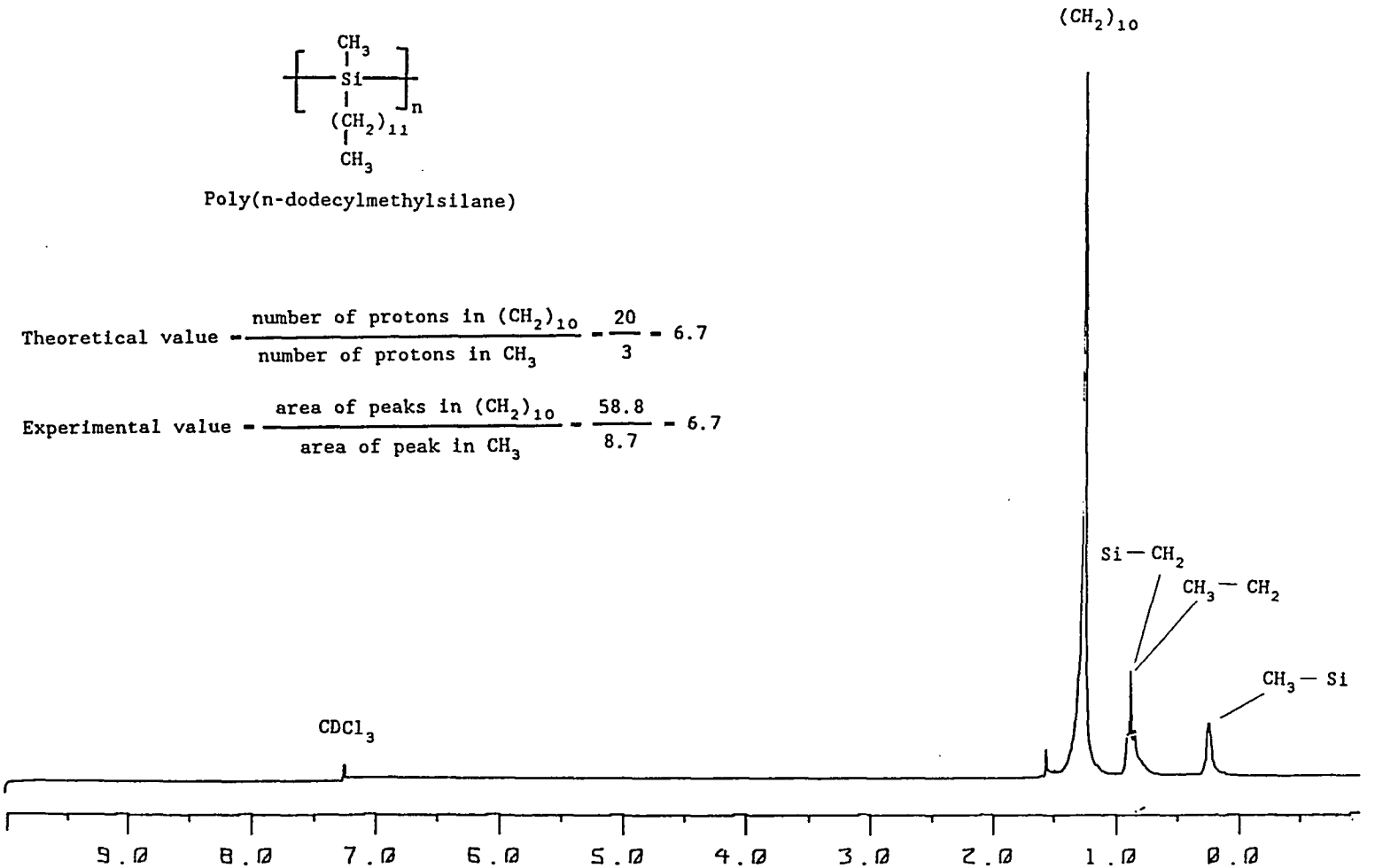


Fig. 3-4 ^{13}C NMR spectrum of poly(n-dodecylmethylsilane) in $CDCl_3$

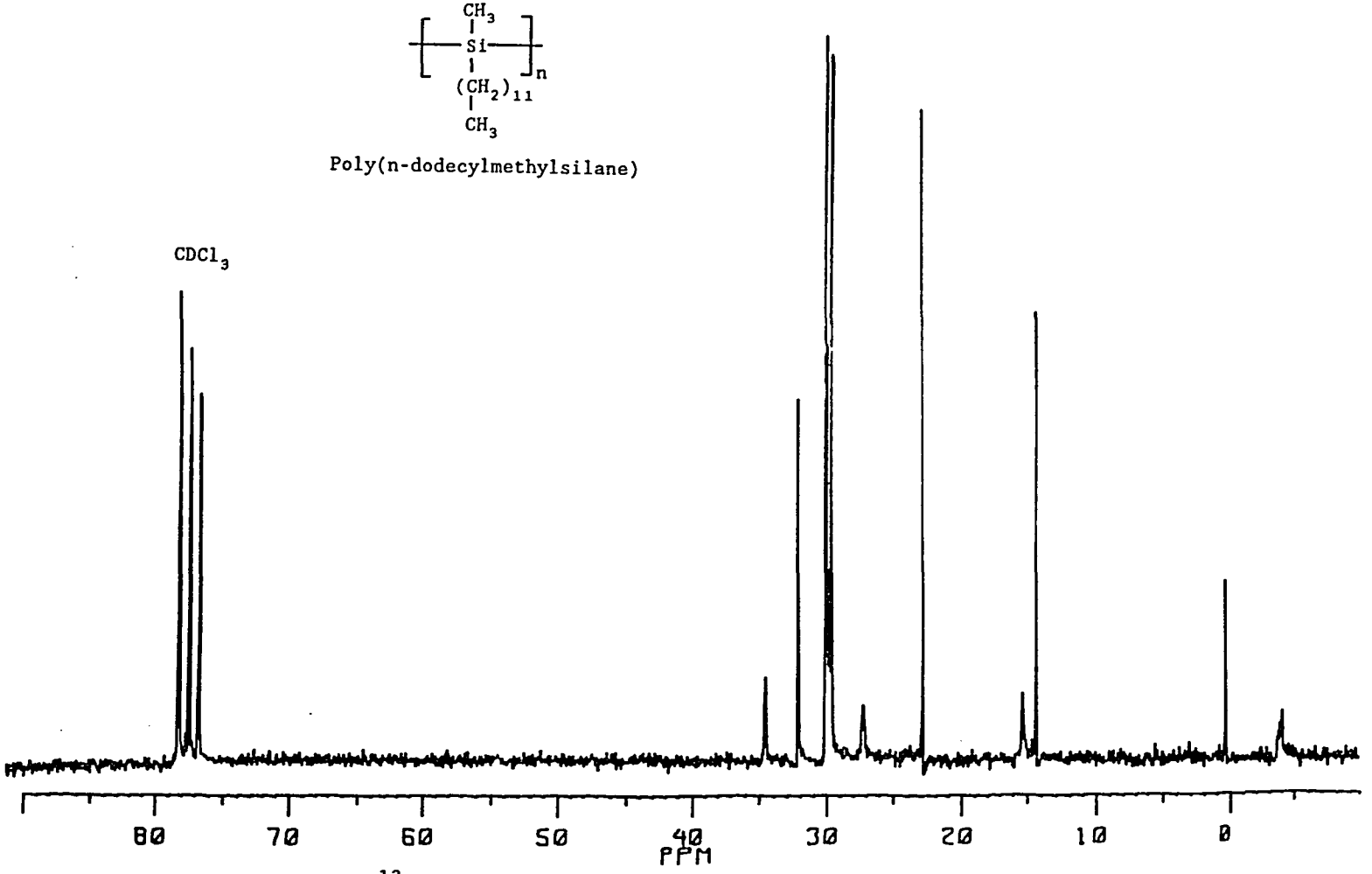


Fig. 3-5 ^{13}C NMR spectrum of poly(n-dodecylmethylsilane) in $CDCl_3$

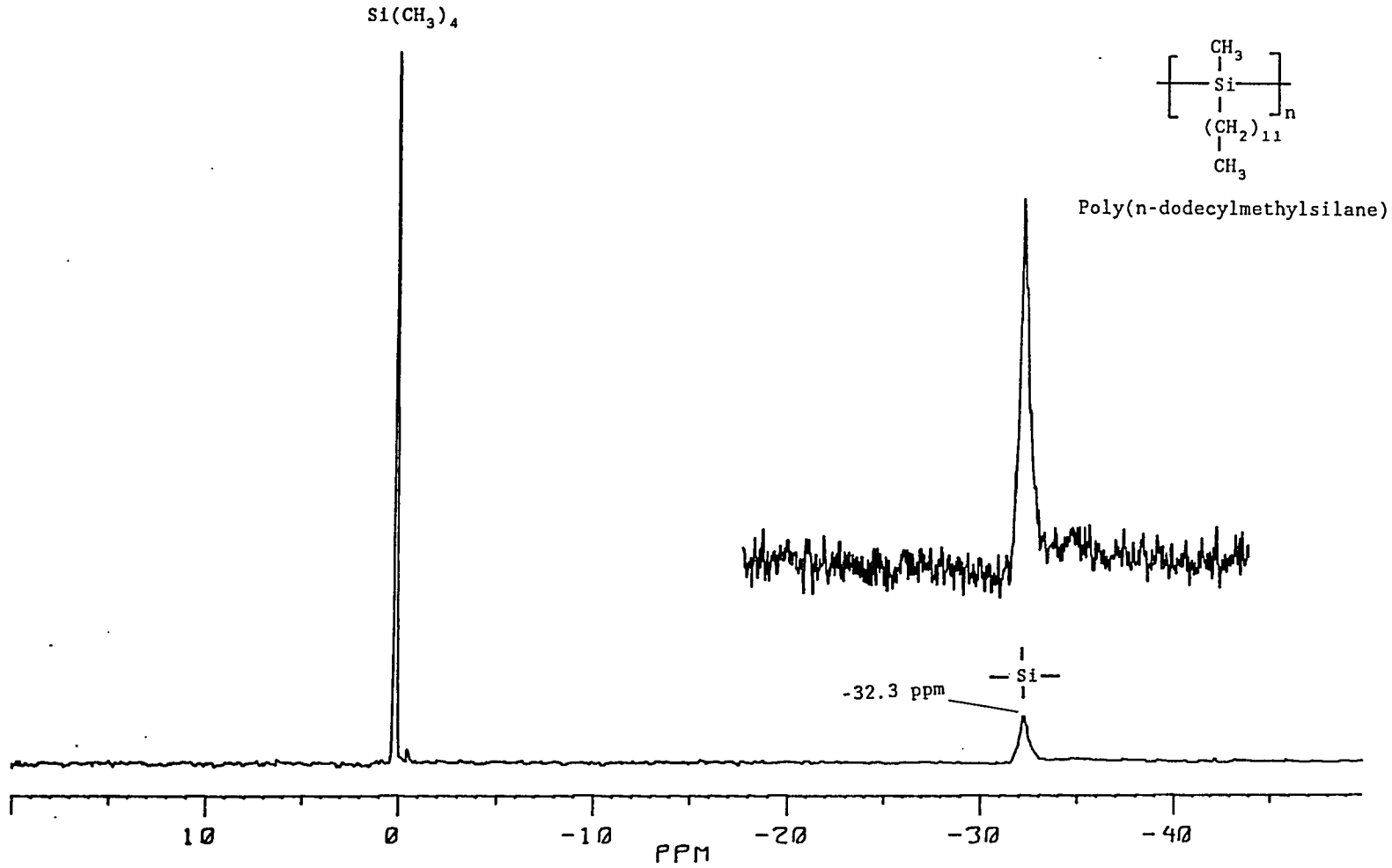


Fig. 3-6 ^{29}Si spectrum of poly(n-dodecylmethylsilane) in $CDCl_3$

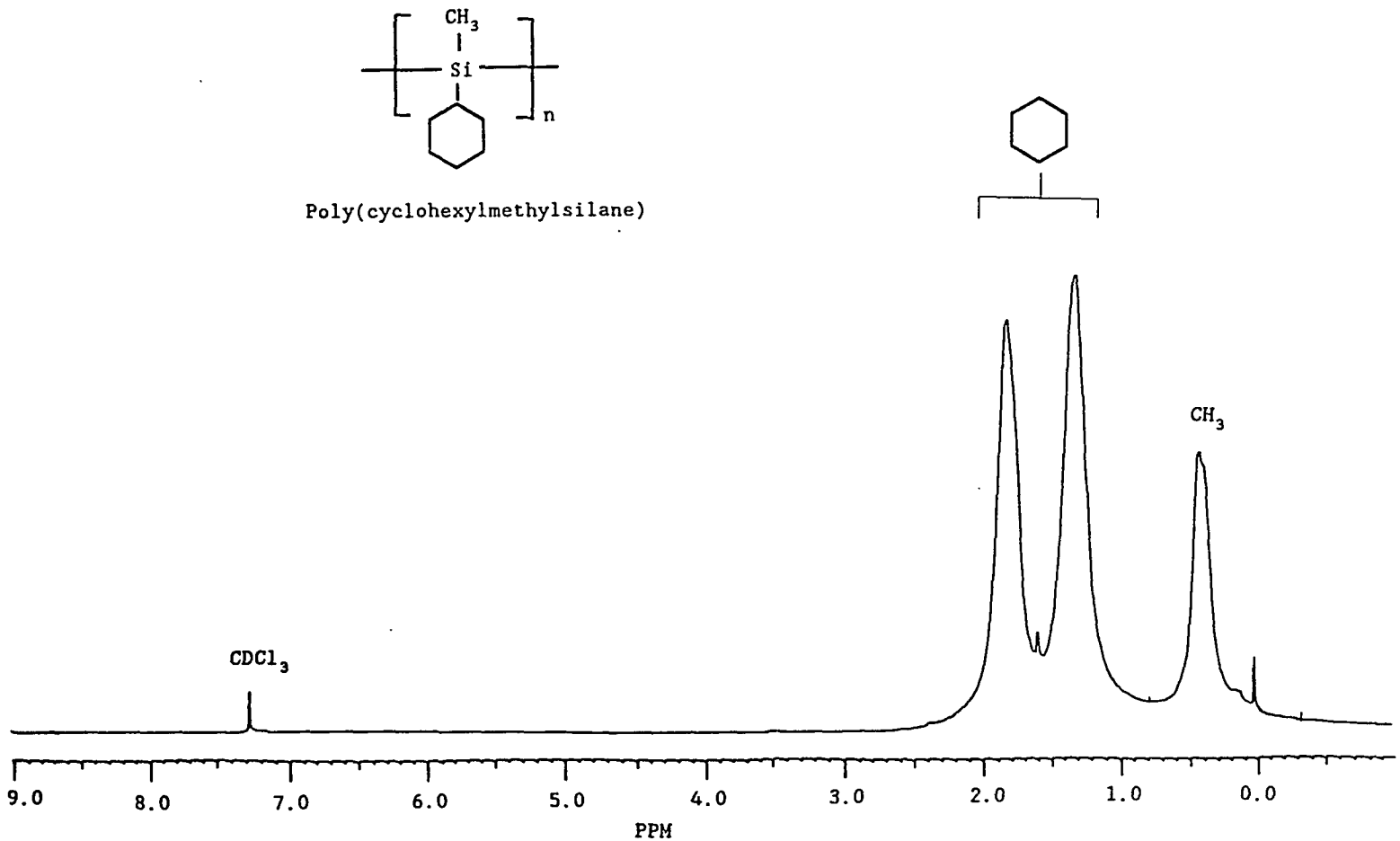


Fig. 3-7 ^{1}H NMR spectrum of poly(cyclohexylmethylsilane) in $CDCl_3$

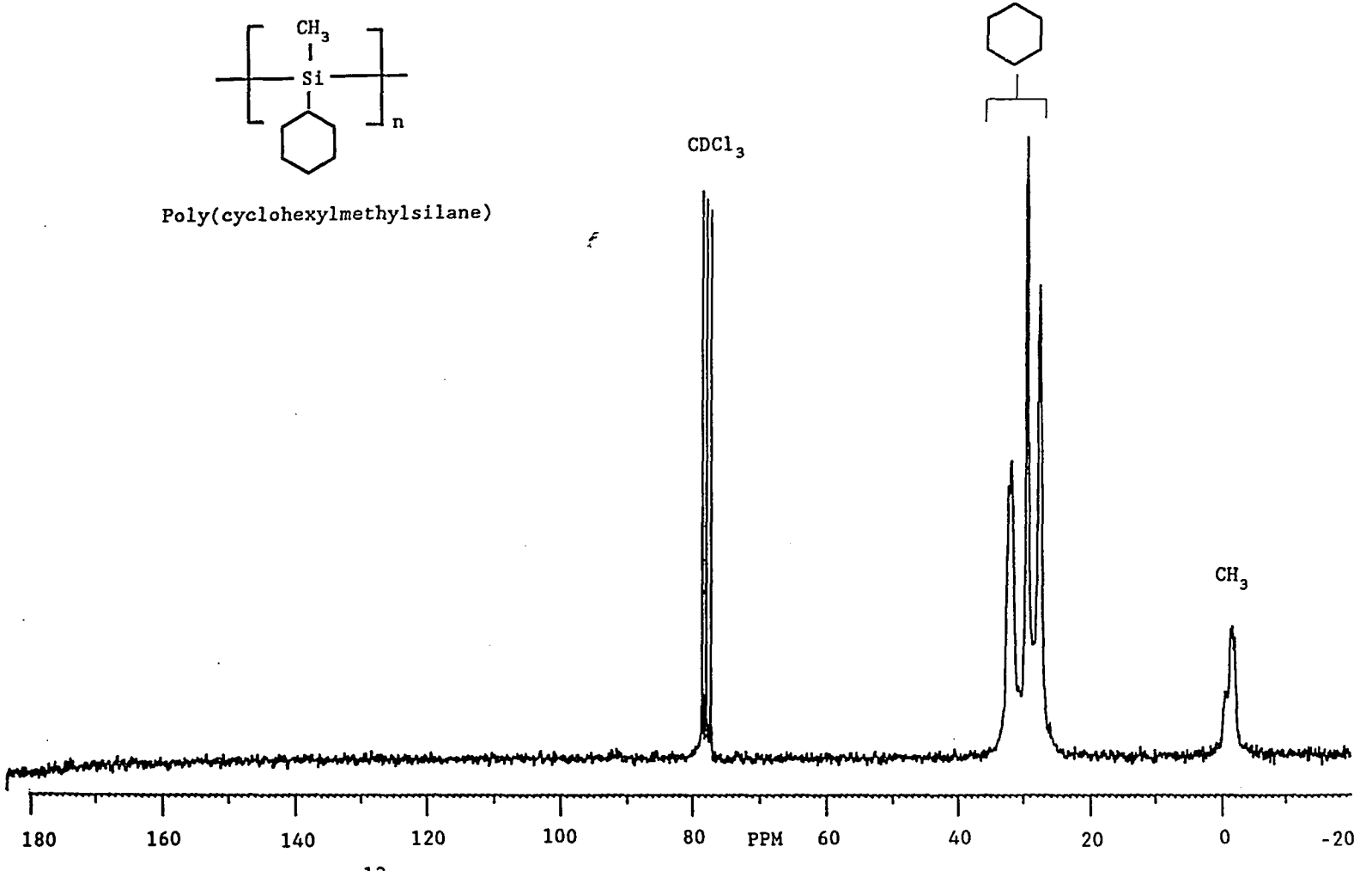


Fig. 3-8 ^{13}C NMR spectrum of poly(cyclohexylmethylsilane) in $CDCl_3$

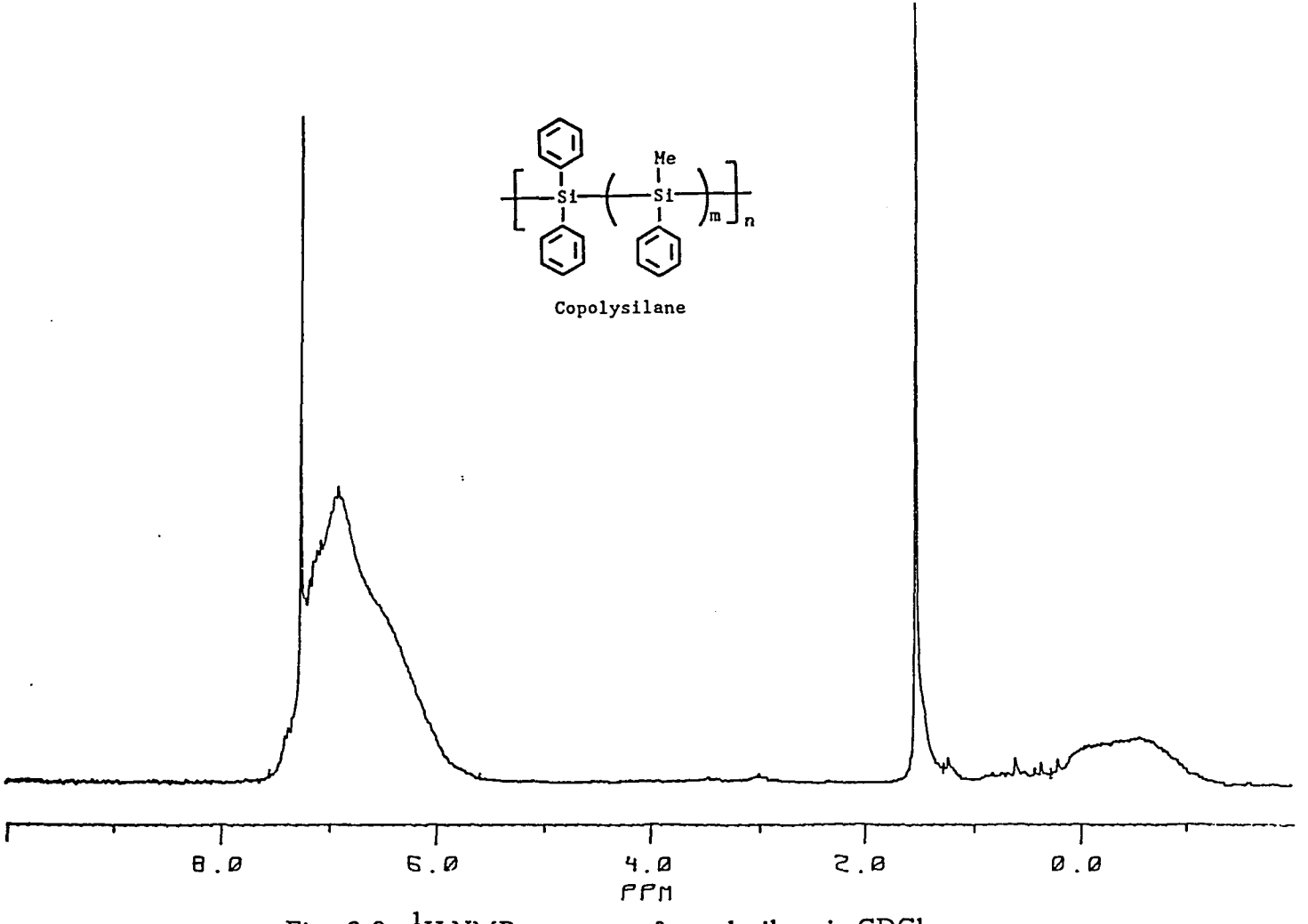


Fig. 3-9 ^{1}H NMR spectrum of copolysilane in $CDCl_3$

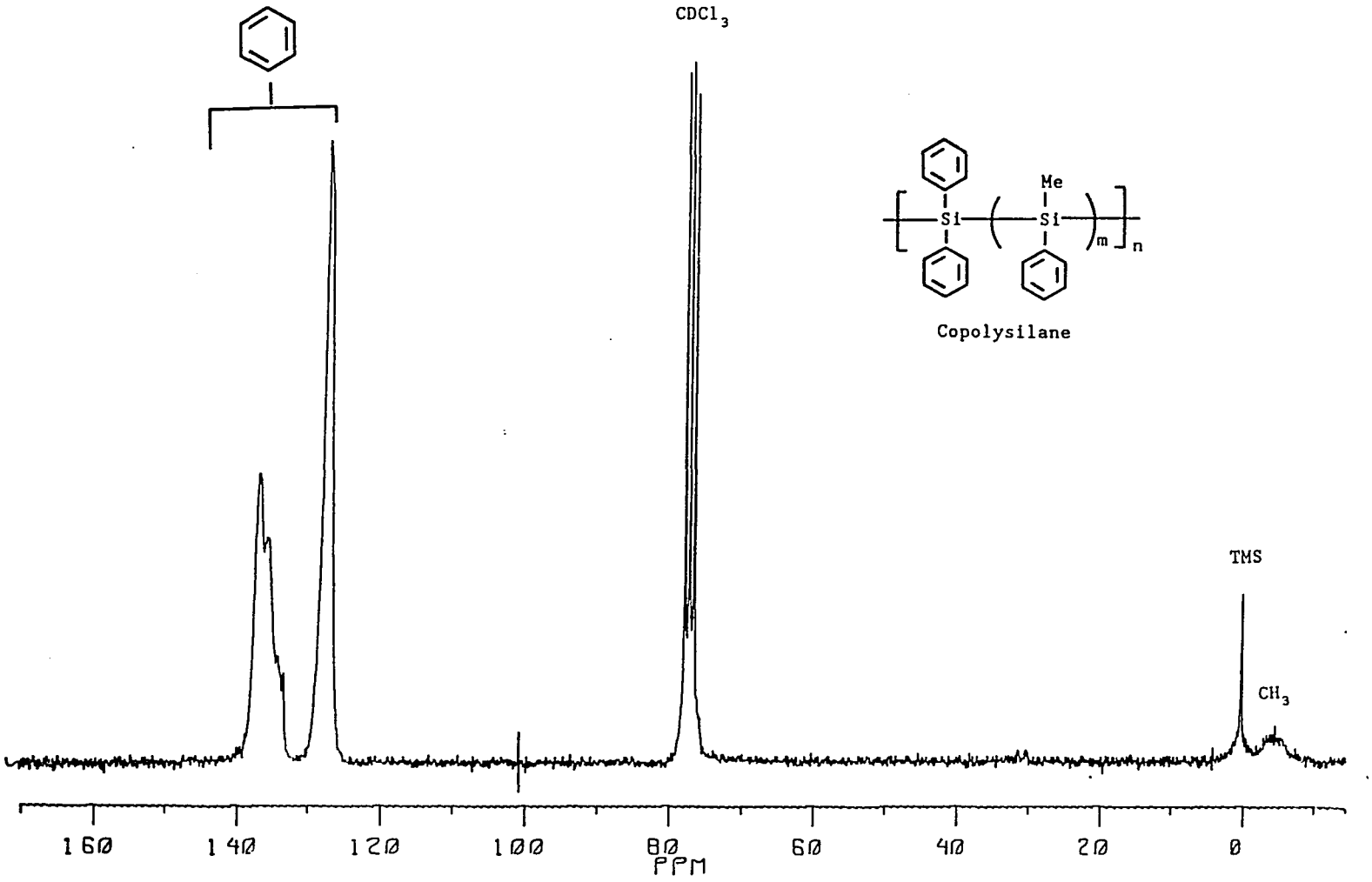


Fig. 3-10 ^{13}C NMR spectrum of copolysilane in $CDCl_3$

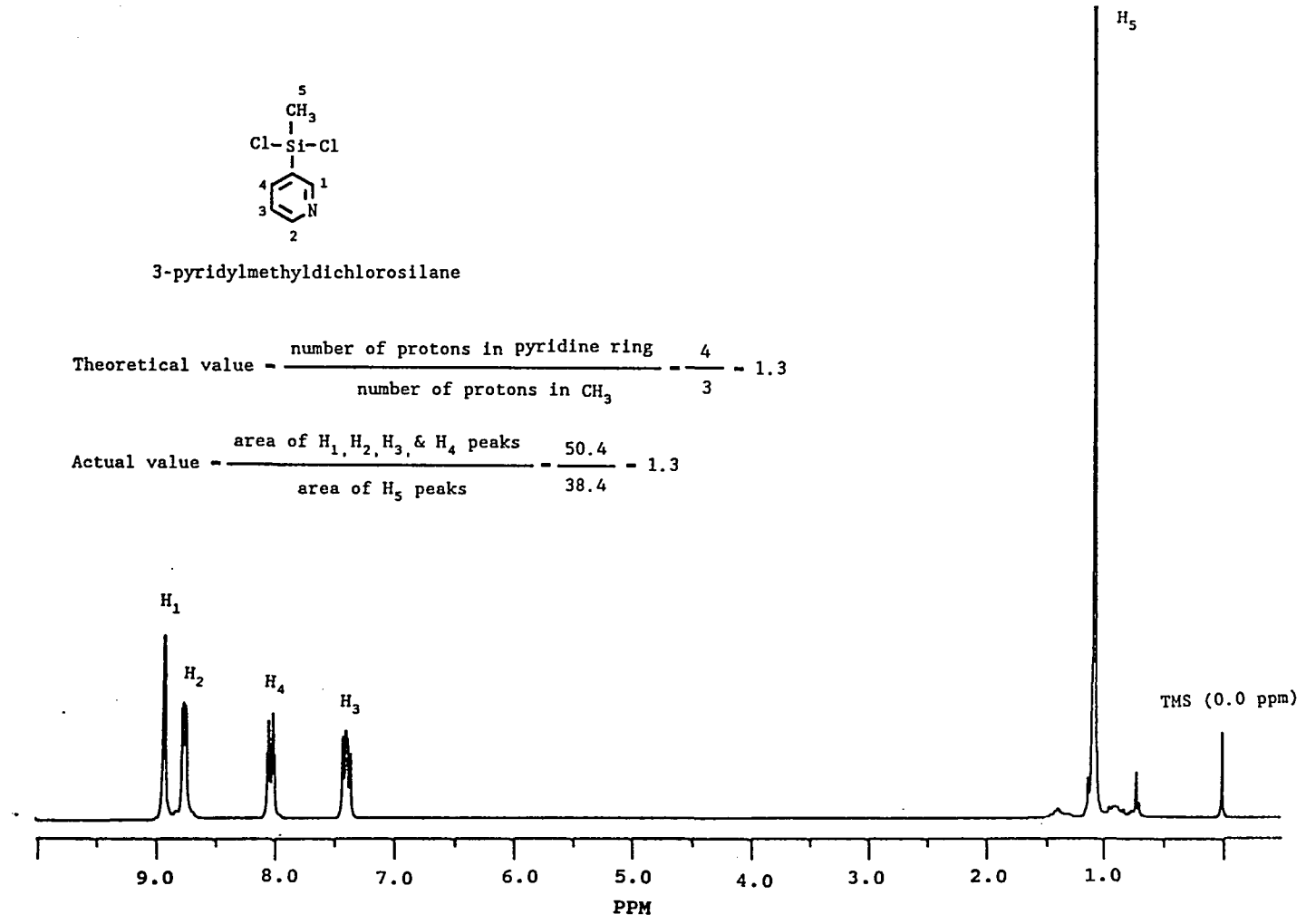


Fig. 3-11 ^{1}H spectrum of 3-pyridylmethyldichlorosilane in $CDCl_3$

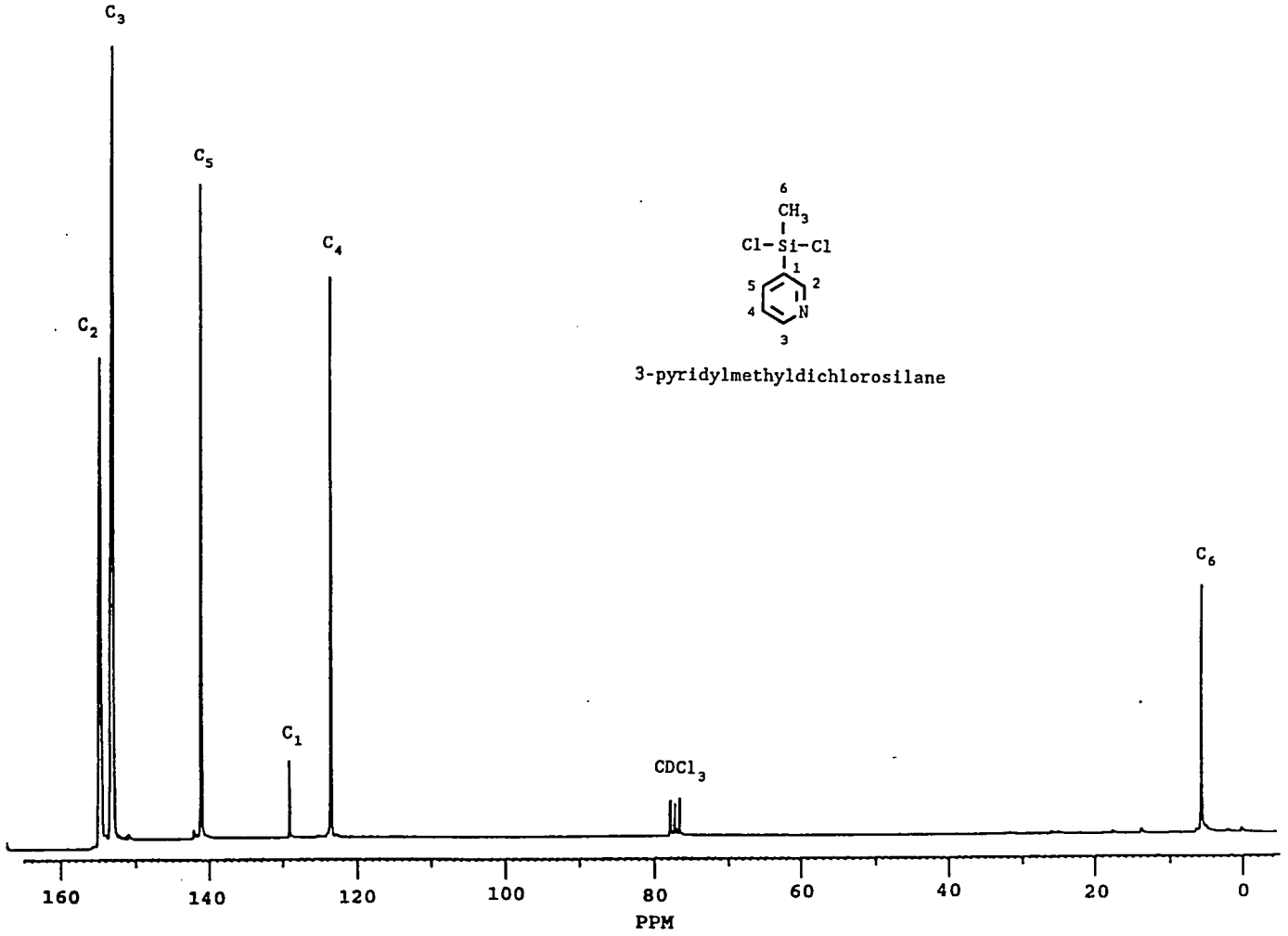


Fig. 3-12 ^{13}C NMR spectrum of 3-pyridylmethyldichlorosilane in $CDCl_3$

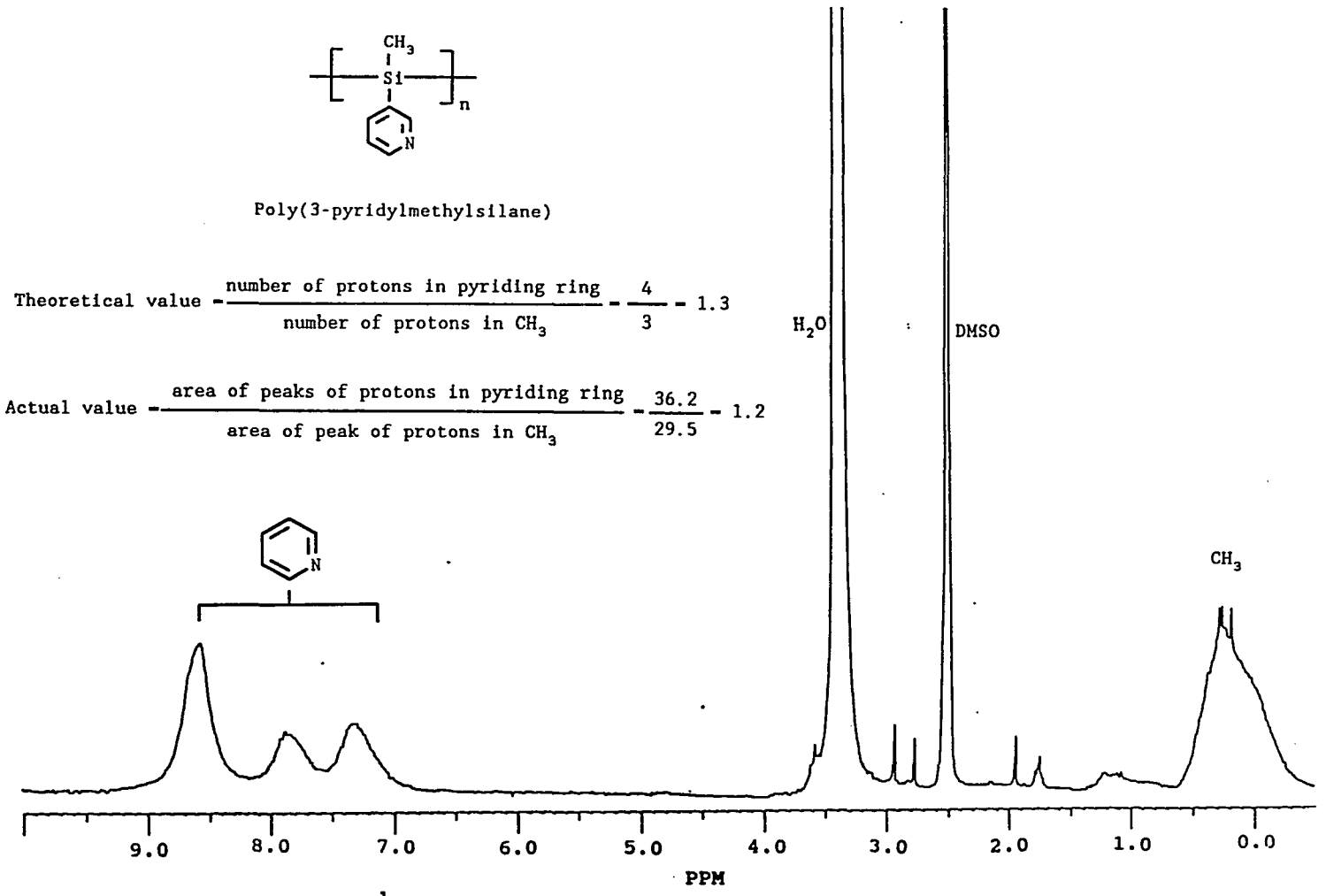


Fig. 3-13 ^{1}H NMR spectrum of poly(3-pyridylmethylsilane) in DMSO

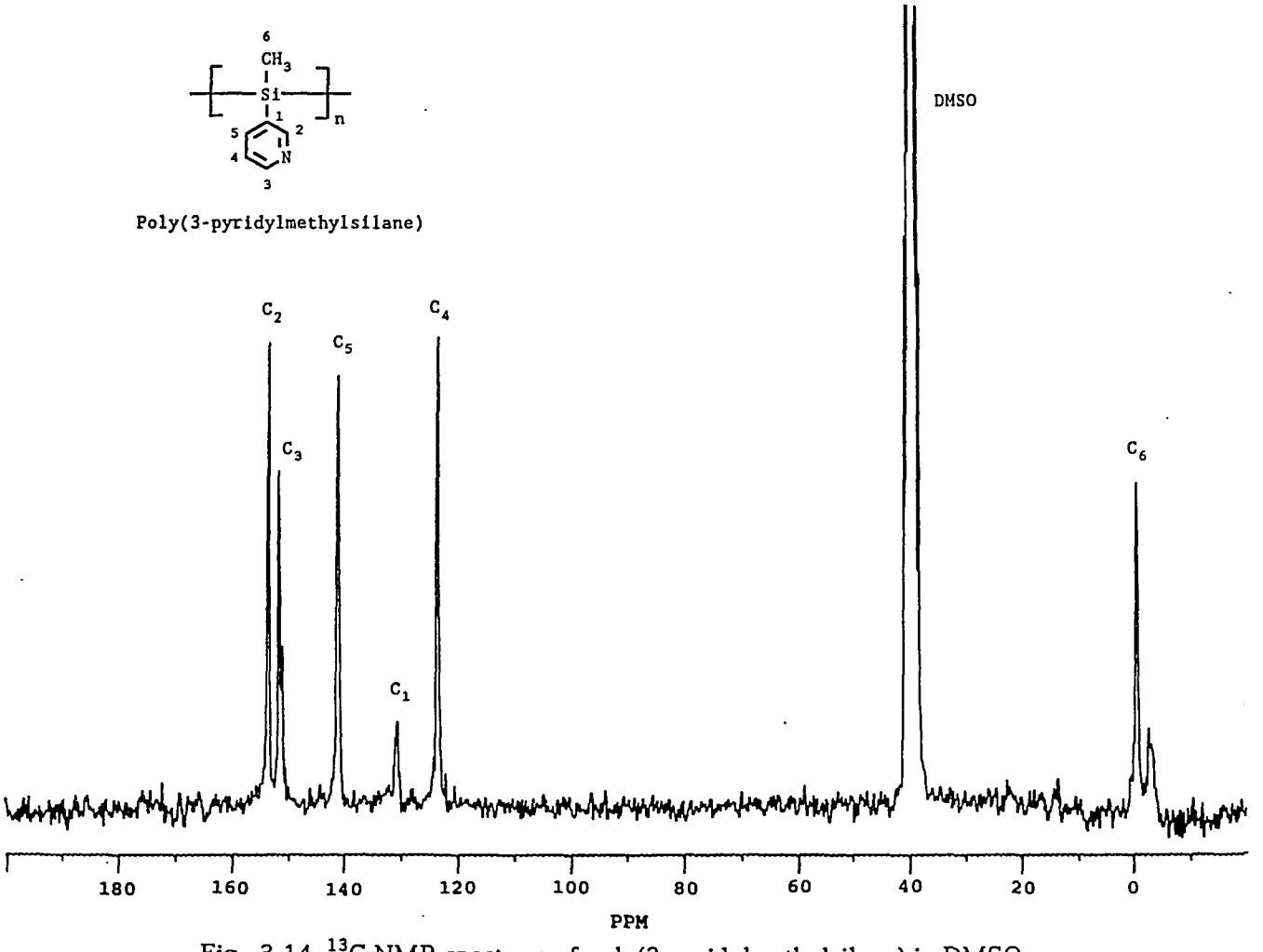


Fig. 3-14 ^{13}C NMR spectrum of poly(3-pyridylmethylsilane) in DMSO

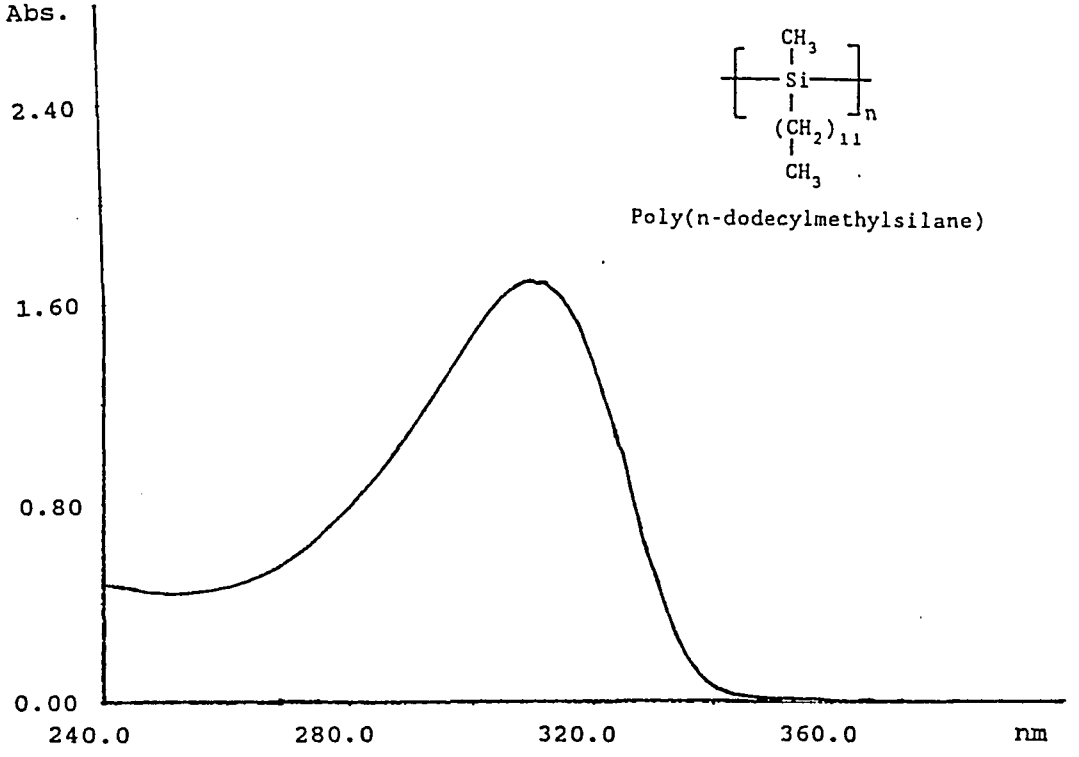


Fig. 3-15 UV spectrum of poly(n-dodecylmethylsilane) in THF (1.9×10^{-4} g/ml)

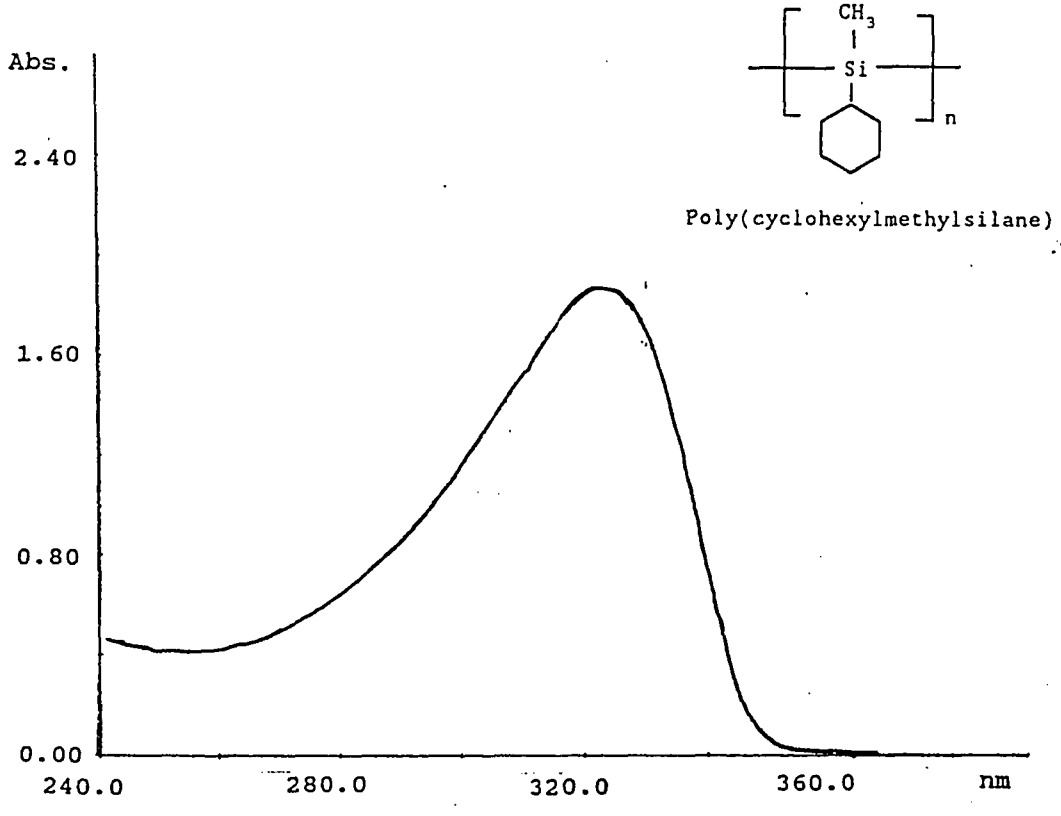


Fig. 3-16 UV spectrum of poly(cyclohexylmethylsilane) in THF (1.9×10^{-4} g/ml

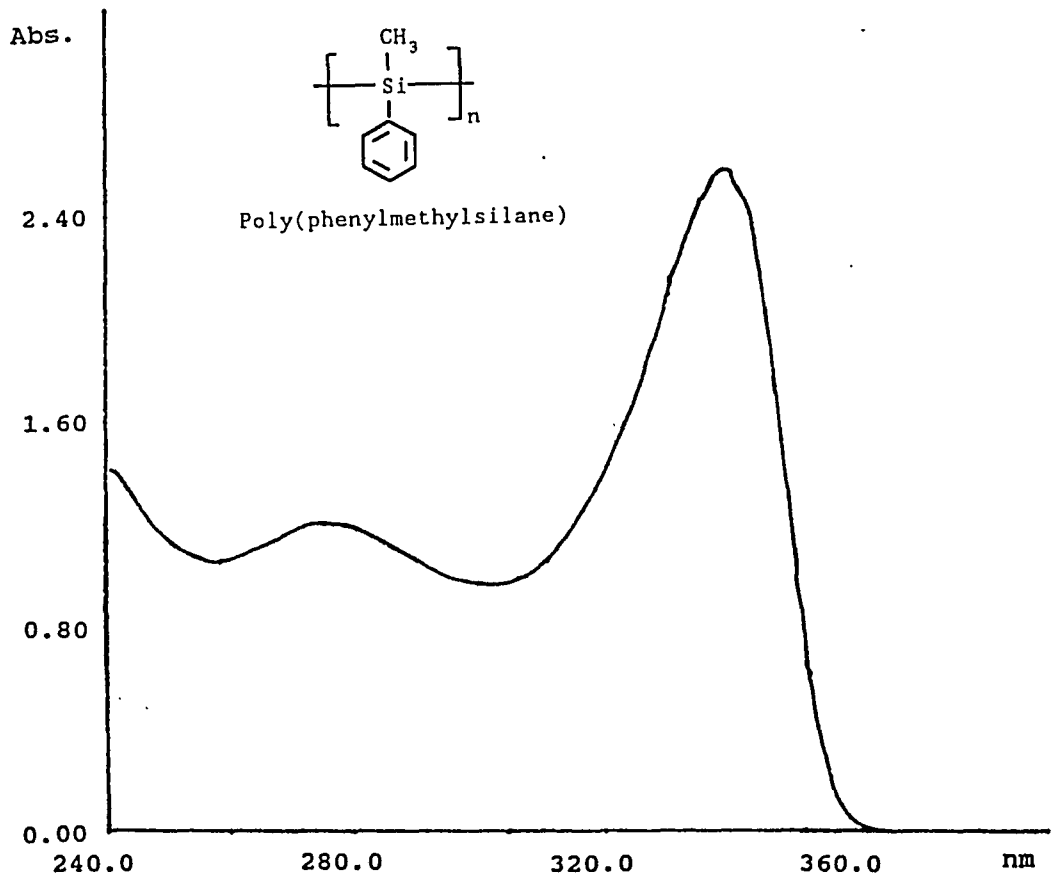


Fig. 3-17 UV spectrum of poly(phenylmethylsilane) in THF (1.9×10^{-4} g/ml)

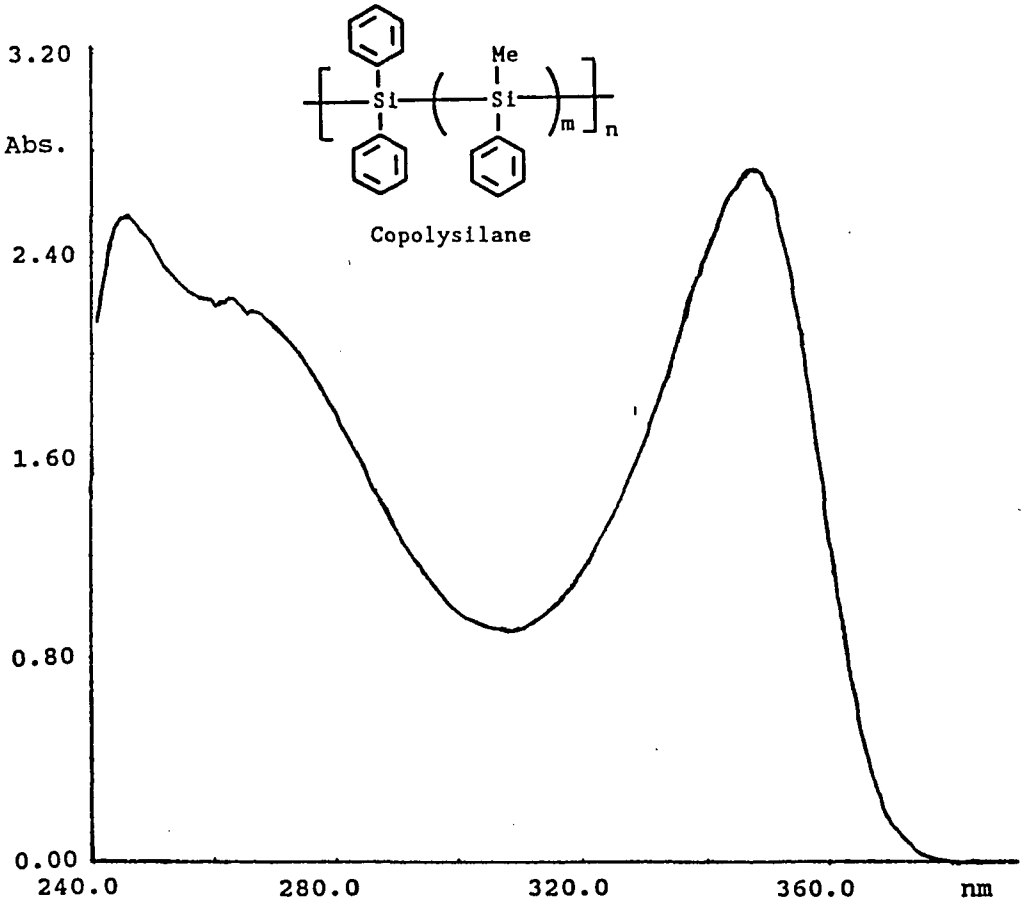


Fig. 3-18 UV spectrum of copolysilane in THF (1.9×10^{-4} g/ml)

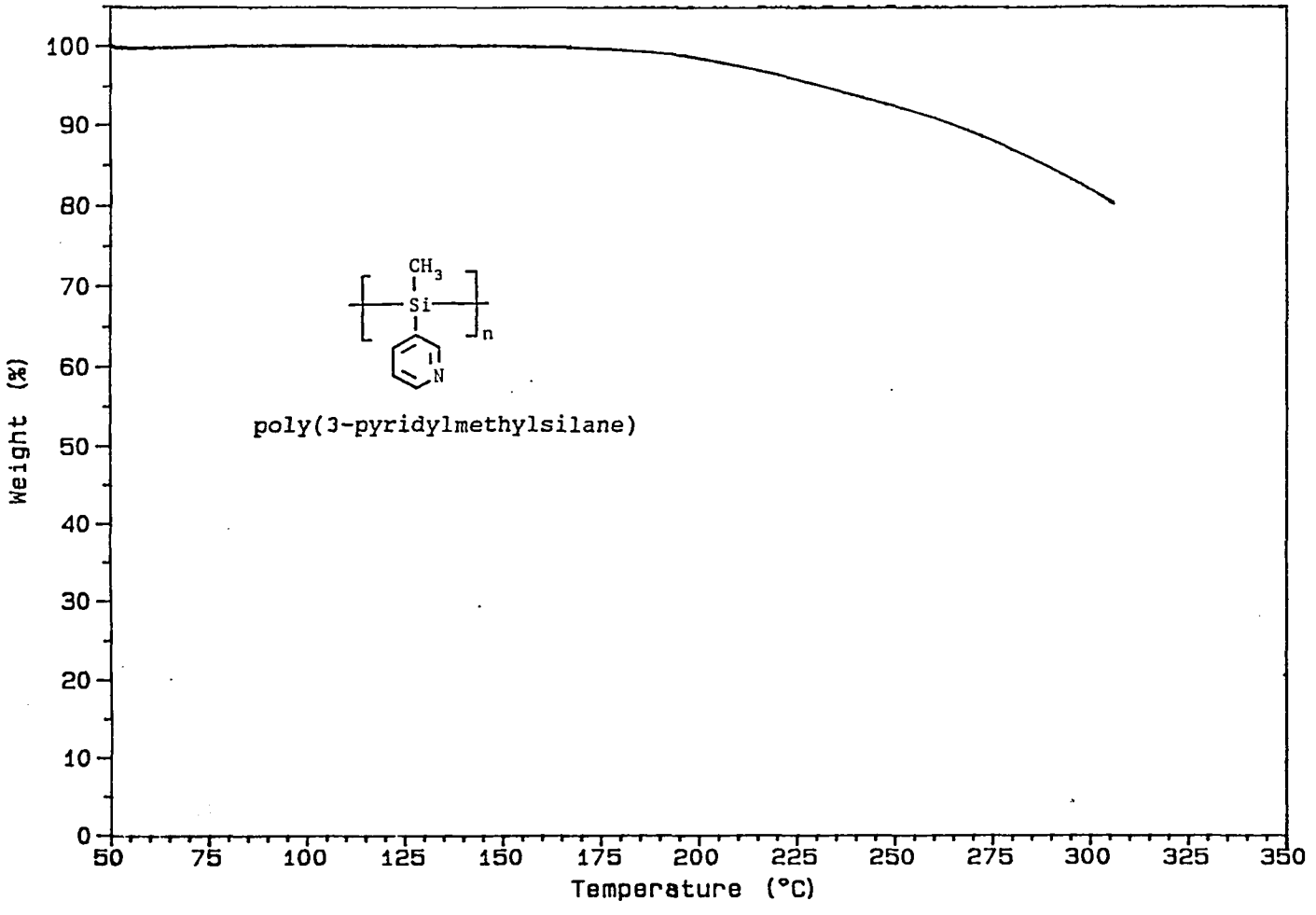
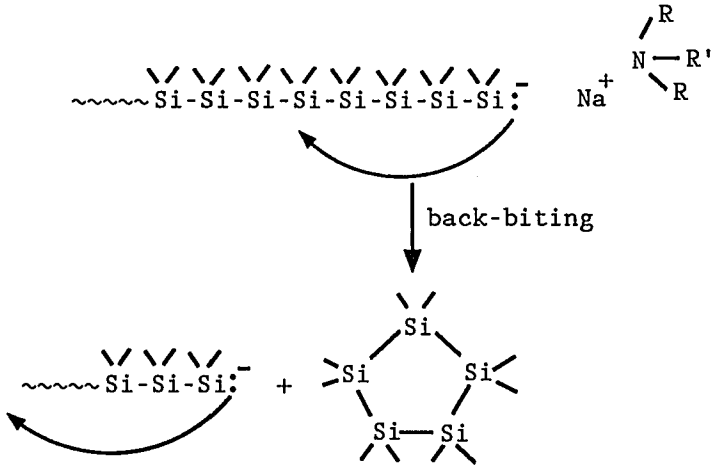


Fig. 3-19 TGA thermogram of poly(3-pyridylmethylsilane)

3.3.3. Determination of Molecular Weight of Poly(3-pyridyl-methylsilane) by VPO

The molecular weight of Poly(3-pyridylmethylsilane) obtained from VPO measurement is $\overline{Mn} = 2.5 \times 10^3$. GPC determination using DMF as a solvent was unsuccessful. The molecular weight of this polymer is quite low due to the degradation of polymer in the process of polymerization. There are a few possible explanations for this observed phenomenon. First the polar solvent (N,N-diisopropyl-ethylamine) can increase the reactivity of silyl anions and causes a back-biting (degradation) process which leads to the formation of cyclic oligomers.[38] The possible mechanism of the degradation is shown below:



A second explanation is that polysilanes can be degraded by an excess of alkali metal in a polar solvent.[39] Still another possible explanation is that the reductive coupling proceeds by the reaction of silyl anions with dichlorosilane

via a chain growth process. At the level of tetra-, penta-, or hexasilane, the anionic center present at one end may react with its chloroterminated end instead of with a monomer.[40] This end-biting process can also leads to the formation of cyclic oligomers.

The rate of degradation strongly depends on the substituents at silicon atom, solvent, alkali metal, reaction time and temperature. Polar solvent, "too high" reactivity of substitutes at silicon, and high temperature will strongly increase the rate of degradation.

3.3.4. Thermal Stability of Poly(3-pyridylmethylsilane)

Figure 3-19 shows the TGA curve of this polymer; no weight loss (degradation) was observed at temperature lower than 180 °C.

3.3.5. Nonlinear Optical Properties of Polysilane

(i). Ultrafast Time Response of Optical Nonlinearity in Poly(phenylmethylsilane)[24]

The value of the third order nonlinear susceptibility $\chi^{(3)}$ was measured to be on the order of $2.0 \pm 0.6 \times 10^{-12}$ esu for the poly(phenylmethylsilane) thin films using OKG experiment.[24] The third order nonlinear response was measured to be faster than 3 psec arising from electronic mechanism. The third order nonlinear susceptibility $\chi^{(3)}$ of poly(phenylmethylsilane) solutions was determined by DFWM experiment[24] to be $1.6 \pm 0.2 \times 10^{-12}$ esu. This value is in

good agreement with the value obtained from OKG experiment.

The observed large value of $\chi^{(3)}$ of poly(phenylmethylsilane) most likely arises from the electrons delocalized along the polymer backbone and from the transition dipole moments parallel to the molecular axes. The fast decay (< 3 psec), which is unresolved by our measurements, indicates an electronic contribution.[40,41] Our results show that polysilane polymers may be potential a new class of materials for applications in nonlinear optics distinct from π-conjugated polymers. They have several advantages over their π-bonded carbon counter part. The main absorption peak due to σ-σ^*transitions is in the UV region. This material is transparent in the visible region. The absorption band can also be shifted by changing the molecular weight, the conformation of the silicon backbone, or the substituents groups so that the resonance enhancement of nonlinear effects at particular wavelengths is possible. Their thin film formation with optical quality suitable for waveguides, as well as the possibility of optical circuits design, render them promising candidates for use in integrated optics.

(ii). Sign of χ^3 in Poly(phenylmethylsilane)[28]

The sign of $\chi^{(3)}$ of the solution were determined to be negative at 532 nm and positive at 1064 nm from Z-scan measurements.[28] The values of $\chi^{(3)}$ at 532 nm is 7.0×10^{-12} esu and negative, while $\chi^{(3)}$ at 1064 nm is relatively small, 5.0×10^{-13} esu, and positive. These values suggest that

$\chi^{(3)}$ at 532 nm is enhanced by a resonance process, although both 532 and 1064 nm are in the transparent region of single-photon absorption. Closer examination shows that there are two main transitions peaking near 3.7 and 4.6 eV in the linear absorption spectrum of poly(phenylmethylsilane). They have been previously assigned[42] to σ-σ^* and π-π^* transitions, respectively. Recent measurements[43] of the quantum efficiency for carrier generation as a function of photon energy and of the electronic absorption spectrum in poly(phenylmethylsilane) have suggested that the band gap is at 4.6 eV, while 3.7 eV is the peak of an exciton band. Strong two-photon absorption at 532 nm has been observed previously in other polysilanes in birefringence measurements.[44-46] The difference in sign arises from the difference in the physical processes responsible for the nonlinear response at the two wavelengths. The larger negative value of $\chi^{(3)}$ at 532 nm is mostly due to two-photon absorption resonance, while the 1064 nm wavelength is well away from two-photon absorption resonance frequency. Therefor a smaller, faster, and positive $\chi^{(3)}$ due to bond-electronic effects should be expected. The Z-scan value at 532 nm is somewhat larger than the DFWM value ($\chi^{(3)} = 1.6 \times 10^{-12}$ esu) reflecting probably a larger two-photon absorption contribution.

(iii). Near Infrared Optical Response in Polysilanes

The results of an near infrared third order nonlinear susceptibility $\chi^{(3)}$ and response time of the polysilane

solutions measured by DFWM technique are shown in the Table 3-1.

Table 3-1. The third order nonlinear susceptibility $\chi^{(3)}$ and response time measured by DFWM technique

Polymer	$\chi^{(3)}$ (10^{-12}esu)	response (10^{-12}s)	λ(nm)
poly(phenylmethylsilane)	1.3300	< 20	1064
poly(phenylmethylsilane-co-diphenylsilane)	1.3686	< 20	1064
poly(n-dodecylmethylsilane)	1.1305	< 20	1064
poly(cyclohexylmethylsilane)	1.3433	< 20	1064

From DFWM measurements, the near infrared (1064 nm) third order nonlinear optical susceptibility $\chi^{(3)}$ of poly(phenylmethylsilane) solution has been determined to be 1.33×10^{-12} seu. A fast response of $\chi^{(3)}$, <20 ps, has also been measured in this DFWM measurements.

Theoretical estimations and experimental investigations have firmly established that larger electron delocalization is a prerequisite for larger values of the nonlinear coefficients. The value of $\chi^{(3)}$ is proportional to the sixth power of the conjugation length for one dimensional systems, such as polysilanes. For polysilane polymers in solution or atactic materials in the solid state

at ambient temperatures, previous electronic spectra studies[47] show that polysilane derivatives containing only alkyl substituents on the backbone absorb in the region from 300-325 nm (Fig. 3-14 and 3-15) with the larger substituents causing shifts to longer wavelengths. Those polymers with aryl substituents directly bonded to the backbone are spectrally red shifted to 335-350 nm. With the same sidegroups, the absorption peaks shift to longer wavelength as the chain length increases. However, recent studies[48] indicated that the limiting spectral structures observed previously for simple atactic polysilanes both in solutions and in solid state do not represent the intrinsic absorption of the polysilane chain, but instead result from the presence of conformational imperfections (deviations from coplanarity) in the backbone. Therefore, no conclusion can be said about the differences in the chain lengths or conjugation lengths of the polysilanes chosen here, since the values of $\chi^{(3)}_{1064\ nm}$ for different substituents are very close to each other as shown in the table 3-1. The nonlinear response is probably due to the intrinsic nonlinearity of the polysilane polymers, and most likely arises from the contributions of the σ-electrons delocalized along the backbone.

We also attempted to measure $\chi^{(3)}_{1064\ nm}$ from thin films. There was no detectable signal in both measurements even when the intensity reached such high values (200 GW/cm^2), coursing film damage. The film is probably too thin to obtain a detectable signal.

3.4. Conclusions

Four polysilanes with different substituents were synthesized: Poly(phenylmethylsilane); poly(phenylmethylsilane- co-diphenylsilane); poly(cyclohexylmethylsilane) and poly(n-dodecylmethylsilane) . The value of the third order optical nonlinearity $\chi^{(3)}$ was measured to be on the order of 2.0 ± 0.6 x 10^{-12} esu from the poly(phenylmethylsilane) thin films using OKG experiment and 1.6 ± 0.2 x 10^{-12} esu from the poly(phenylmethyl-silane) solution using DFWM experiment. These values are in good agreement. The response time of nonlinear optical process associated with electronic mechanism is found to be faster than 3 ps..

The sign of $\chi^{(3)}$ of the poly(phenylmethylsilane) solution were determined to be negative at 532 nm and positive at 1064 nm from Z-scan measurements. The values of $\chi^{(3)}$ at 532 nm is -7.0 x 10^{-12} esu, while $\chi^{(3)}$ at 1064 nm is relatively small, +5.0 x 10^{-13} esu.

The near infrared (1064 nm) third order optical nonlinearity of polysilanes has been studied using DFWM technique. Results have shown that $\chi^{(3)}_{1064\ nm}$ is about 1.3 x 10^{12} esu. This value is about one order of magnitude small than that of CS_2. But about two order of magnitude larger than silicon glass fibers,[48] thus it is possible to use polysilane polymers as a fiber nonlinear material. A fast response of $\chi^{(3)}$ <20 ps has also been measured. No significant third order optical nonlinearity difference was

observed with different substituents of polysilanes.

The first polysilane with pyridyl functional group, Poly(3-pyridylmethylsilane) was synthesized and characterized. The molecular weight of this polymer obtained from VPO measurement is $\overline{Mn} = 2.5 \times 10^3$. GPC determination using DMF as a solvent was unsuccessful. The molecular weight of this polymer is quite low due to the degradation of polymer during the process of polymerization. The rate of the degradation strongly depends on the solvent, alkali metal, reaction time and reaction temperature. It is possible to increase the molecular weight of this polymer by decreasing reaction temperature, using coordination additives such as diglyme or 15-crown-5 ether, and change the solvent.

Chapter IV. Synthesis and Characterization of π - Electron Conjugated Polymers and Their Nonlinear Optical Properties

4.1. Introduction

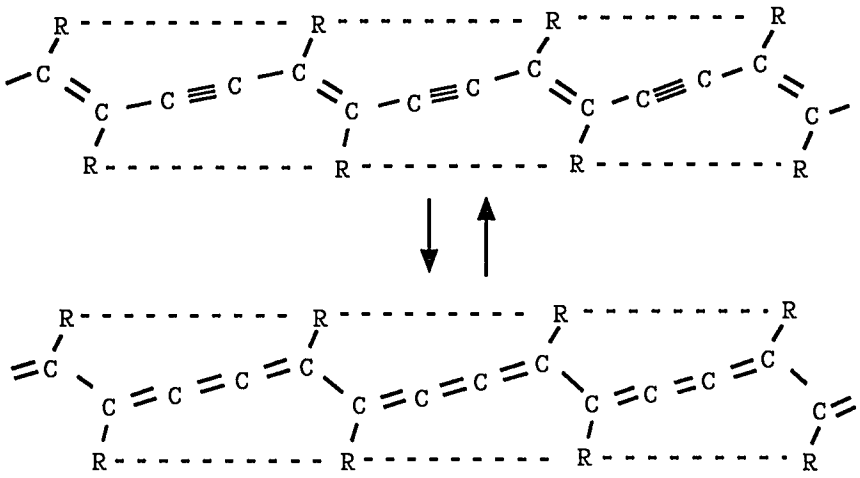
Organic polymeric materials containing π-electron conjugated molecular structure have been shown to exhibit ultrafast, and very large nonlinear optical response.[1-3] This rapidly growing area of research may lead to promising applications of polymeric materials in optoelectronic devices ranging from optical computing to sensor protection.[1,3-5] Numerous theoretical calculations predict that optical nonlinearity in π-electron systems are dramatically affected by the π-electron delocalization length in the polymer systems.[6-8] The degree of π-electron delocalization is mainly determined by the effectiveness of *p*-orbital overlap in the polymer chain.[9,10] To optimize the optical properties, maximum overlap is required.[5,9-13]

Although Conjugated polymers exhibit the largest non-resonant third order susceptibilities $\chi^{(3)}$ to be found in the range $10^{-9} \sim 10^{-10}$ esu with response times in femtoseconds, the magnitudes of $\chi^{(3)}$ are still too small for practical applications. The requirement of third order susceptibilities $\chi^{(3)}$ for optical devices applications theoretically calculated approaches 10^{-9} esu or higher. Other problems including the inherent deficiencies of these materials, such as poor solubility, poor thermal and

environmental stability and high optical absorption losses, prevent their immediate use in practical applications. The application of polymer systems in devices would require two areas to be developed further: (1) enhancement of non-resonant $\chi^{(3)}$, as mentioned above; (2) improvement of physical properties such as solubility, mechanical strength, and thermal stability etc..

The goal of our work described this chapter is to synthesize π-conjugated polymers using novel synthetic routes and to make high quality optical clear films and single crystals for nonlinear optical properties investigations. Three different π-conjugated polymers were prepared.

Polydiacetylenes have been among the most intensely studied organic materials exhibiting significant optical nonlinearity.[1] These polymers have traditionally been prepared using solid-state, free-radical polymerization scheme introduced by Wegner.[14] The polymer backbone is planar, and fully conjugated, best represented in most cases as:



The structure of the backbone is a resonance mixture of the acetylenic and the butatriene structures.[15-17] The substituents groups R include paraffins, alcohols, and carboxylic acids etc.. Most polydiacetylenes are insoluble in common organic solvents,[18] or in more exotic organic solvents,[19] causing difficulties in processing these materials into desired forms such as films. Since a new class of soluble polydiacetylenes-poly(4-butoxycarbonyl-methylurethane) (poly-4BCMU) has discovered by G. N. Patel[20] in 1978, an explosive rebirth of interest has been developed for nonlinear optical applications in the emerging field of ultrafast optical signal processing and all optical communication technologies.

Poly-bis(p-toluenesulfonate) is another important polydiacetylene that is widely investigated for nonlinear optical applications due to the following reasons: (i) It is among the few diacetylenes which polymerize quantitatively upon thermal annealing or a low dosage of radiation, while

most of other diacetylenes require a high dosage of radiation for quantitative polymerization; and (ii) Large single crystals can be readily grown from solution.

As discussed previously, optical nonlinearity in π-electron systems increases with increasing π-electron delocalization. Electron delocalization depends upon orbital overlap between π-orbitals on adjacent atoms. From these considerations Dalton pointed out ladder polymers,[6] with their planar configuration and uninterrupted π conjugation should exhibit the molecular conformation necessary for orbital overlap and hence maximum electron delocalization. These observations are supported by recent theoretical calculations and these systems are expected to be the most likely candidates to yield large nonlinear optical susceptibilities.[9] Another factor greatly influencing the physical properties of conjugated polymers is its environmental stability. Most of the linear conjugated polymers (such as polythiophene, poly-p-phenylene and polyacetylene, etc.) are unstable in air and their physical properties (such as conductivity and third order nonlinear optical properties) are easily degraded by the interruption of π-electron delocalization.[21] Ladder type polymers , however, have an advantage over linear polymers due to their double strand and rigid rod chain structures. The conjugated systems in ladder polymers are locked into a plane. They possess high resistance to mechanical, thermal and chemical degradation as would be intuitively expected for a double strand chain structure and as predicted by

theoretical calculations.[22] However, ladder polymers have major problems associated with their special structures, e.g. poor solubility, particularly in organic solvents. This is especially true for ladder polymers with delocalized π-electron systems because of strong Van der Waals interactions between the π-electron clouds on adjacent polymer chains. Theoretical calculations on polybenzimidazobenzophenanthroline (BBL) have shown that π-π Van der Waals interaction between adjacent chains is even stronger than chemical bonding.[23] This intrinsic insolubility greatly inhibits the characterization and processing of these materials.

The nonlinear optical properties of poly-4BCMU in polymethylmethacrylate (PMMA) matrix films have been studied by us.[24,25] The third order optical nonlinearity $\chi^{(3)}$ and response time of poly-4BCMU in matrix films have been measured using picosecond and femtosecond optical Kerr effect (OKE)[26] and optical phase conjugation (OPC).[27] The relaxation time of the transient degenerate four-wave mixing grating in poly-4BCMU in matrix films has been also measured using a mode-locked YAG laser system producing 30 picosecond pulses of 60 MW peak power at 530 nm.[25] Laser experiments were performed by Dr. Lina Yang and Dr. P. Ho at the Institute for Ultrafast Spectroscopy and Lasers and Photonic Application Laboratory, the City College of The City University of New York.

4.2. Experimental

4.2.1. Synthesis of 4-Butoxycarbonylmethylurethane (4BCMU) Monomer

4BCMU monomer was prepared via the following scheme[20]:

$$2\ HO\text{-}(CH_2)_4\text{-}C{\equiv}CH + \frac{1}{2}\ O_2 \xrightarrow[THF,\ 25°C]{catalysts} 2\ HO\text{-}(CH_2)_4\text{-}C{\equiv}CH\rightarrow_2$$

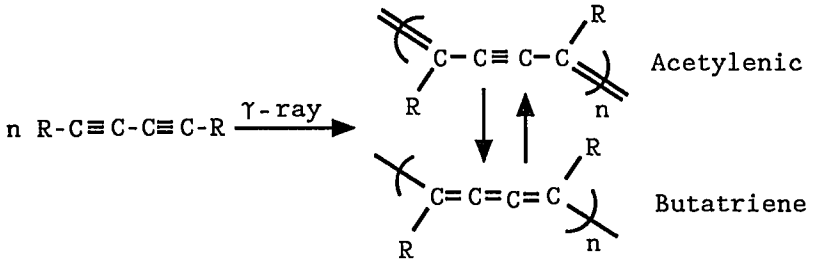
$$2\ H_3C\text{-}(CH_2)_3\text{-}OCOCH_2\text{-}NCO + 2\ HO\text{-}(CH_2)_4\text{-}C{\equiv}CH\rightarrow_2 \xrightarrow[THF,\ 25°C]{catalysts}$$

$$H_3C\text{-}(CH_2)_3OCOCH_2NHCOO\text{-}(CH_2)_4\text{-}C{\equiv}C\rightarrow_2$$

A 500 ml 3-necked round bottom flask was fitted with a magnetic stirrer, an addition funnel, a thermometer and placed in a cold water bath with heat at 25 °C. 5-Hexyn-1-o1 (4.908 g, 0.05 mole) and 200 ml tetrahydrofuran were added to this flask. Then 0.05 g of dibutyltindi-2-ethylhexanoate and 1 ml of triethylamine were added as catalysts under stirring. Butylisocyanatoacetate (14.0 ml, 10.125 mole) was added dropwise over a period of 30 minutes and allowed to react for 2 hours at 25 °C, and then, the resulting solution was poured into 1500 ml of hexane under stirring for purification. The precipitate obtained was filtered and dried under vacuum. Finally, 1.348 g (21.1% crude yield) of product was obtained. The product was further purified by recrystallization twice from acetone/hexane (4/1) mixed solvents and dried under vacuum in the dark.

4.2.2. Solid State Polymerization

Solid state polymerization was performed by 1.4-addition polymerization using high energy γ-ray irradiation.



Where $R=-(CH_2)_4OOCHNCH_2OCO(CH_2)_3CH_3$

One gram of 4BCMU monomer was added to 25 ml of methanol and stirred for one hour. The insoluble red colored particles of poly-4BCMU, formed by thermal annealing during storage, were filtered out. Colorless filtrates containing 4BCMU monomer were transferred to a crystallization dish for evaporation at room temperature for 48 hours in the dark to obtain colorless monomer crystals. These 4BCMU crystals were irradiated for 24 hours with gamma rays to obtain metallic green-gold colored poly-4BCMU. The gamma source used for this procedure was a 10,000 curie J. L. Shepherd, Mark 1, model 68, Cs irradiator.

4.2.3. Preparation of Optical Clear Films of Poly-4BCMU in Polymethylmethacrylate Matrices

High optical transparency, uniform thickness films of poly-4BCMU in polymethylmethacrylate (PMMA) matrices were prepared in a large crystallization dish with controlled

vapor pressure of the methylene chloride solvent. UV absorbance of about 0.7 at 530 nm and 620 nm wavelength was obtained by using different poly-4BCMU to PMMA mole ratios. The most satisfactory ratio and concentration matching the requirements of this film absorption are shown in the Table 4-1.

Table 4-1. Ratio of poly-4BCMU with PMMA and concentration in methylene chloride

Wavelength (nm)	530	620
Absorption (A)	~ 0.7	~ 0.7
*Ratio (wt.%)	4.5 - 5.5	0.7 - 1.5
**Concentration (wt.%)	1.5 - 2.0	7.0 - 8.0

$$*\text{Ratio} = \frac{\text{poly-4BCMU}}{\text{PMMA}} \times 100\ \%$$

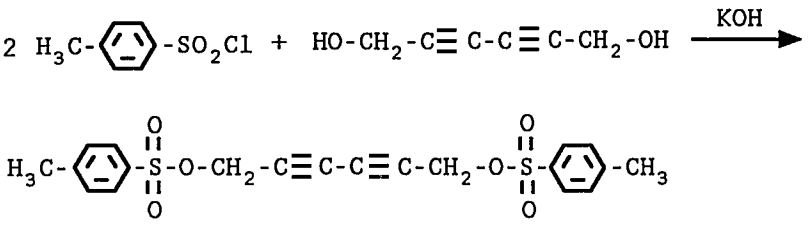
$$**\text{Concentration} = [(\text{poly-4BCMU} + \text{PMMA})/CH_2Cl_2] \times 100\ \%$$

Poly-4BCMU was dissolved in methylene chloride for 24 hours; and PMMA, in methylene chloride for 48 hours. The system of a large crystallization dish with controlled vapor pressure of the methylene chloride solvent was first allowed to reach equilibrium with respect to vapor saturation. The required ratio and concentration as shown in Table 4-1 of mixed solutions of poly-4BCMU and PMMA solutions were then introduced to glass slides with minimum exposure to ambient atmosphere. Solidification took place in about one hour. Film samples were allowed to evaporate further at ambient

conditions then sealed for laser experiments.

4.2.4. Synthesis of 2,4-hexadiyn-1,6-bis(p-toluene-sulfonate) Monomer

2,4-Hexadiyn-1,6-bis(p-toluenesulfonate) (PTS) was prepared via the following scheme:



The procedure used for the synthesis of PTS was essentially that of G. N. Patel[20] with slight modifications.

2,4-Hexadiyne-1,6-diol (5.5 g, 0.05 mole) was dissolved in 50 ml of tetrahydrofuran and 21 g (0.11 mole) of p-tosylchloride was added to the solution. The solution was cooled to 5 °C using a ice water bath. A cold (5 °C) solution of 6.5 g (0.11 mole) potassium hydroxide in 20 ml of water was added dropwise with vigorous stirring. After the addition of potassium hydroxide solution, the mixture was stirred for additional 3 hours at 5 °C and was then poured into 250 ml of ice water. Crystals of the bis-(p-toluenesulfonate) was precipitated and filtered at that temperature. The product was washed with methanol and dried under vacuum. The crude product of PTS was purified by recrystallization from acetone/hexane (1/2) at 5 °C. Finally, 12.8 g (60% yield) of the PTS crystals were

obtained, (mp 90-91 °C).

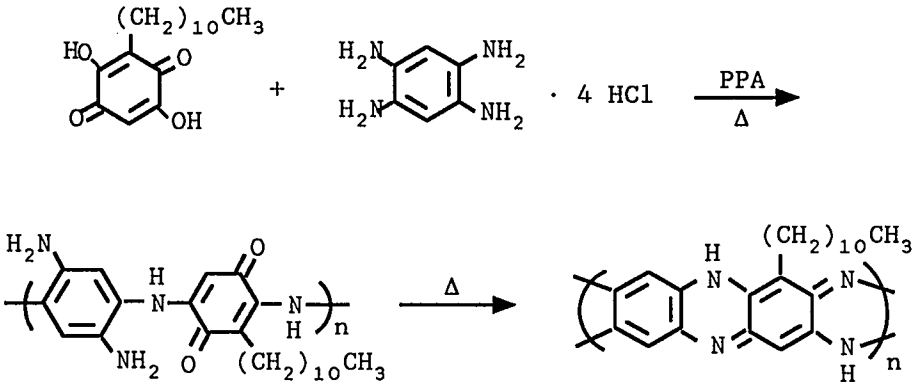
4.2.5. Preparation of Thin Film Single Crystals of Poly-PTS

Thin film single crystals were prepared by the solution-shear growth method.[28] The schematic diagram of solution-shear apparatus is shown in Figure 4-1.

PTS monomer (0.3 g) was dissolved in 1.5 ml of distilled acetone and filtered though a 0.5 μm filter. The clean shear growth apparatus was kept in an air-tight bag with drierite for about 30 min. The bag and shear growth apparatus was placed in an ice box and cooled for about 1 hour at 0 °C. A few drops of the solution were placed in the interface between two optically flat quartz substrate surfaces. The bag was filled with nitrogen gas again to displace any oxygen and allowed to stand for 1.5 hours at 0 °C, and then shear via a linear slow translation of one of the substrate with respect to the other at a shear rate of 1 mm/sec. The pressure utilized in the solution-shear growth was approximately 0.5 pounds/sq. inch and the evaporation was continued for 60 hours at 20 °C subsequent to initial seeding for 5 hours at 0 °C. The solution-shear growth was carried out under nitrogen atmosphere and in a darkroom condition since PTS monomer tends to become more reactive in the oxygen atmosphere and even visible light is sufficient to induce polymerization. The thin film single crystals of PTS thus prepared were approximately 4x7 millimeter in area and about one micrometer in thickness. The polymerization was affected by UV radiation for two minutes.

4.2.6. Synthesis of Soluble Ladder Polymer

Ladder polymers have traditionally been prepared by polycondensation.[6] A soluble ladder polymer was prepared by the condensation of the aromatic tetramines 1,2,4,5-tetraminobenzene tetrahydrochloride and 2,5-dihydroxy-3-undecyl-p-benzoquinone (Embelin).



The method of the preparation of prepolymer (intermediate) was essentially that of J. K. Still and E. L. Mainen.[29]

To a polyphosphoric acid solution prepared from 70 g of phosphoric acid and 10 g of phosphorus pentoxide was added 1.155 g of 1,2,4,5,-tetraaminobenzene tetrahydrochloride dissolved in 10 g of phosphoric acid. The temperature of the mixture was raised to 140 °C to allow the complete displacement of hydrogen chloride. When the evolution of gas ceased (ca. 1 hour), the ring closure were carried out at 200 °C for 4 hr. in a rotating flask under reduced pressure (0.1 mm). The black powder

polymer obtained are soluble in common solvents, such as THF, chloroform, DMSO and DMF.

4.2.7. NMR Characterization of Poly-4BCMU, Poly-PTS, and Ladder Polymer

^{1}H and ^{13}C NMR spectra were obtained with a IBM WP-200 SY Fourier Transfer NMR Spectrometer operated at 200 MHz for proton using Bruker software. The chemical shifts were referenced to tetramethylsilane ($SiMe_4$) at 0 ppm for ^{1}H NMR spectra and chloroform-*d* ($CDCl_3$) at 77 ppm for ^{13}C spectra.

4.2.8. UV Spectroscopy of Poly-4BCMU in PMMA Matrix Films

The UV spectra were obtained on a Varian DMS 300 UV Visible Spectrophotometer.

4.2.9. FT-IR Spectroscopy of Ladder Polymer

The FT-IR spectrum was obtained on a Bio-Rad FT-IR Spectrophotometer, Model FTS-40.

4.2.10. Thermal Stability of Ladder Polymer

The thermal stability of ladder polymer was determined by TGA techniques with a DuPont Thermal Analyzer, Model 990. The sample size of ladder polymer was 4.5 mg. The heating rate was 10 °C/min. from 50 °C to 350 °C under the atmosphere of nitrogen.

4.2.11. Photomicroscopy of Poly-PTS Single Crystal Films

The photomicrographs of Poly-PTS were obtained with a

HFM automatic photomicrographic system.

4.2.12. Ultrafast Nonlinear Optical Processes of Poly-4BCMU in PMMA Matrix Films[24]

The third order optical nonlinearity $\chi^{(3)}$ of poly-4BCMU in PMMA matrix films was measured using Optical Phase Conjugation (OPC).[24,27] Three second harmonic 530 nm 30 picosecond beams derived from a quantum mode-locked Nd:YAG oscillator/ amplifier laser system were used in this measurements. Two counterpropagating beams overlapped in the nonlinear medium. A third probe beam irradiated the overlap region. The interaction of the three beams produced a backward signal wave phase conjugate to the probe wave. The temporal information of polymers was determined by time delaying the backward counterpropagating beam. Seven samples of poly-4BCMU in PMMA matrix films were used in this study.

Kinetics of $\chi^{(3)}$ was measured using picosecod (ps) and femtoseconds (fs) Optical Kerr Effect (OKE).[24,26] The transmitted signals through OKE using poly-4BCMU in PMMA matrix films as the Kerr medium. In this measurement, an 8 ps duration 530 nm wavelength laser pulse was used as the pump beam and an 8 ps 1060 nm laser pulse was applied as the probe beam. Further experimental details were described in reference 24.

4.2.13. Intensity Dependence of Picosecond Nonlinear Response Time of Poly-4BCMU in PMMA Matrix Films[25]

Red color films of poly-4BCMU in PMMA matrices were prepared as described in section 4.2.3. The sample absorbance was about 0.7 at 530 nm. The yellow films were obtained through exposing red films to the vapor of trifluoracetic acid (TFA), a hydrogen bond breaking agent.[30] To avoid damaging the sample, single shot laser pulses were used. The time between two successive shots was > 2 minutes. The excitation source was a mode-locked YAG laser system producing 30 ps pulses of 60 MW peak power at 530 nm. The decay time of the degenerate four wave mixing (DFWM)[27] signal was monitored as a function of the intensity. Further details were described in reference 25.

4.3. Results and Discussion

4.3.1. Determination of Structures of 4BCMU Moncmer, Poly-4BCMU, PTS Monomer, and Ladder Polymer by ^{1}H and ^{13}C NMR Spectra

^{1}H and ^{13}C NMR spectra of 4BCMU monomer with their assignments are shown in figures 4-2 and 4-3. Figures 4-4 and 4-5 show the ^{1}H and ^{13}C NMR spectra of poly-4BCMU with their assignments.

The crystals of 4BCMU obtained are very sensitive toward light and heat. Unlike most of the polydiacetylene reported in the literature,[18,19] this polymer is soluble in common organic solvents such as methylene chloride, tetrahydrofuran and chloroform.

The structure of the PTS monomer was confirmed by ^{1}H

and ^{13}C NMR spectra shown in the figures 4-6 and 4-7.

Solid state ^{13}C NMR spectrum of ladder polymer is shown in figure 4-8.

4.3.2. UV Spectroscopes of Poly-4BCMU and Ladder Polymer

Figure 4-9 shows a UV spectrum of poly-4BCMU in PMMA matrix film. It shows this film obtained has an absorption maximum at 530 nm. Typical thickness of this film was about 8±2 μm. Samples thickness was measured using a travelling microscope. The UV spectrum of ladder polymer is shown in figure 4-10.

4.3.3. FT-IR Spectroscopy of Ladder Polymer

FT-IR spectrum of ladder polymer is shown in figure 4-11.

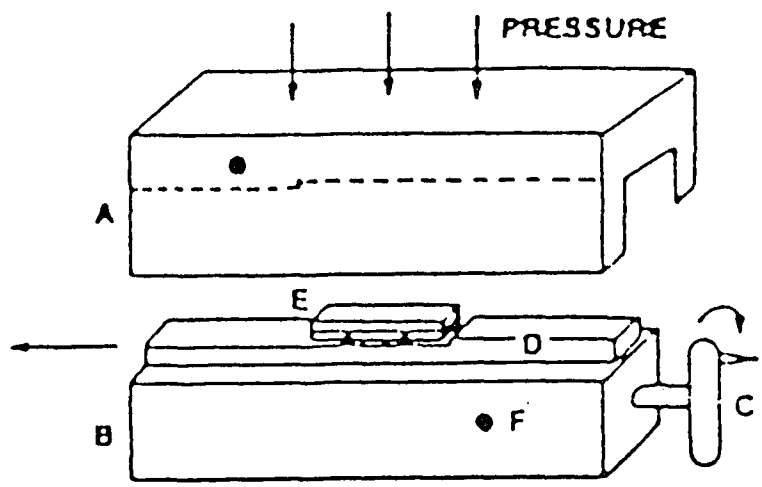
4.3.4. Thermal Stability of Ladder Polymer

Figure 4-12 shows the TGA curve of ladder polymer. This polymer is thermal stable at temperature up to 250 °C under nitrogen atmospheres. This temperature is lower than normal ladder polymers. One of the possibilities of the low thermal stability (250 °C) is that the ring closure was not completed during thermal treatment process.

4.3.5. Photomicroscopy of Poly-PTS Single Crystal Films

The photomicrographs of poly-PTS single crystal are shown in Figure 4-13. Some defects was found on the surface

of crystals that may be caused by the limitation of solution shear apparatus. Modifications of the shear rate and pressure of the apparatus supplied by Institute for Ultrafast Spectroscopy and Lasers and Photonic Application Laboratory of The City College of CUNY has not yet been successful.



A: The top heating plate
B: The base Heating plate having a proper mold design for holding the substrates in place.
C: The d.c. drive attached to the movable platen D.
D: The platen that introduces shear by moving the bottom substrate with respect to the top.
E: The substrates carrying the monomer in the interface.
F: The thermocouple probes of the temperature control unit.

Fig. 4-1 The Schematic of the melt-shear growth apparatus:

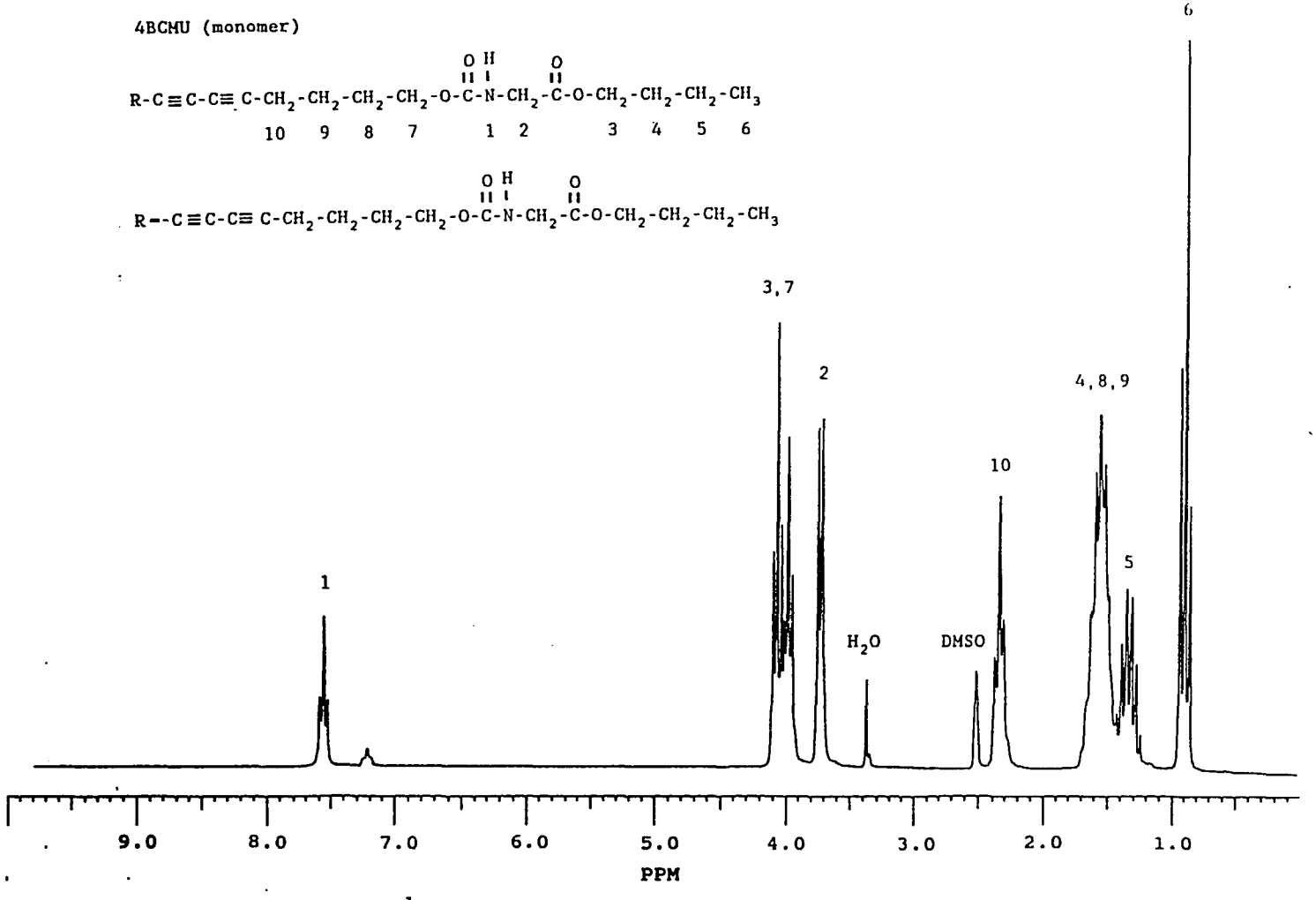


Fig. 4-2 ^{1}H NMR spectrum of 4BCMU monomer in DMSO

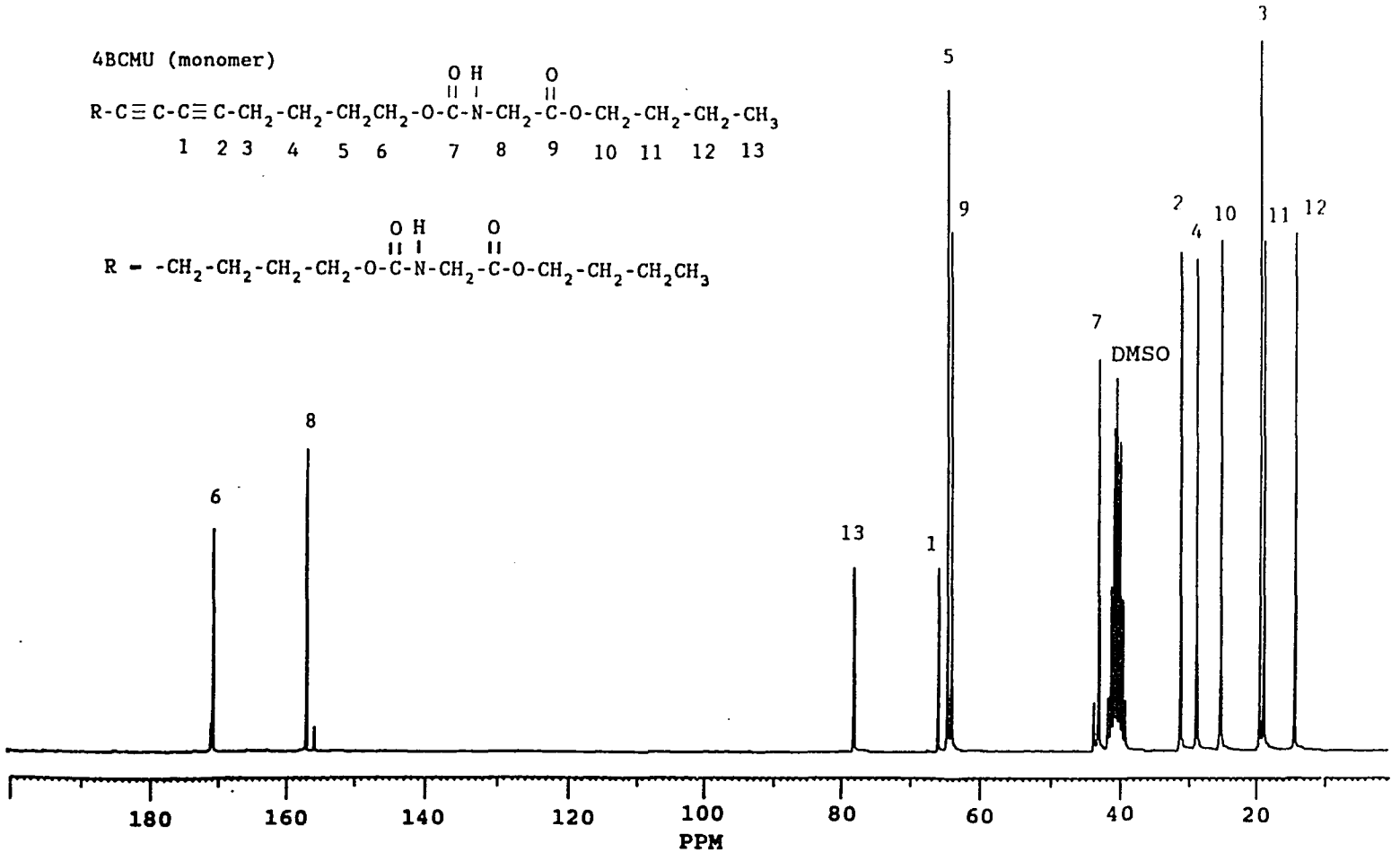


Fig. 4-3 ^{13}C NMR spectrum of 4BCMU monomer in DMSO

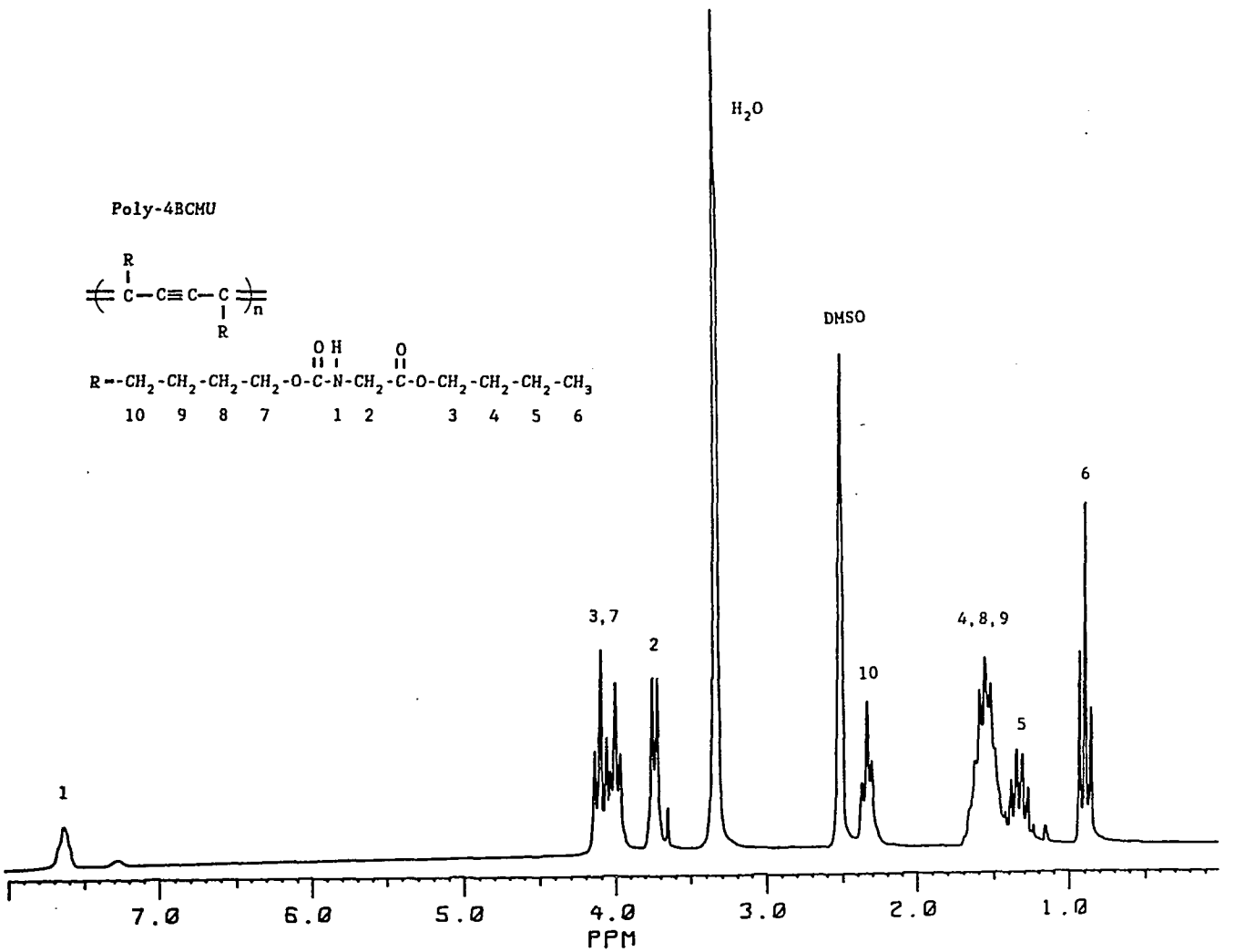


Fig. 4-4 ^{1}H NMR spectrum of poly-4BCMU in DMSO

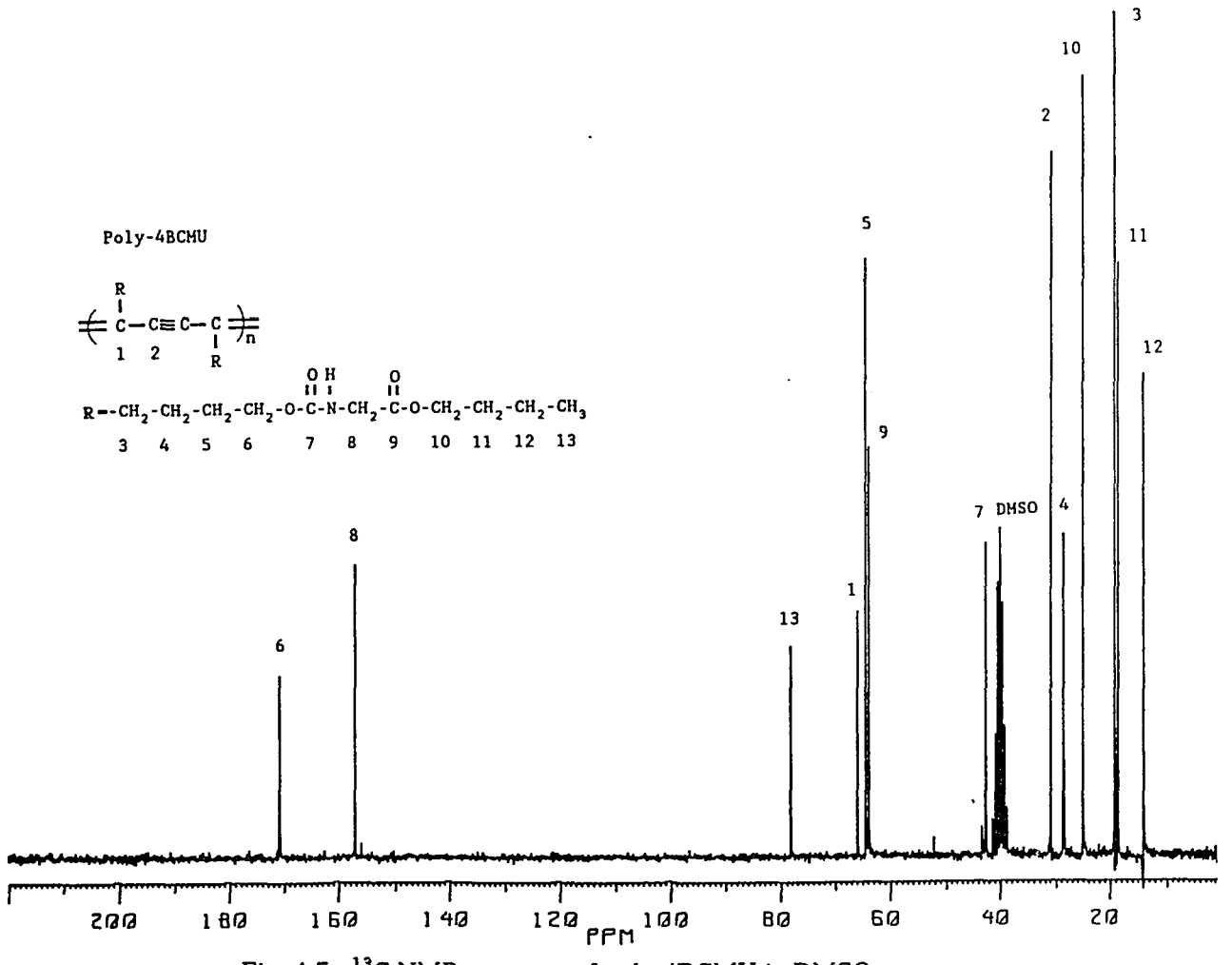


Fig. 4-5 ^{13}C NMR spectrum of poly-4BCMU in DMSO

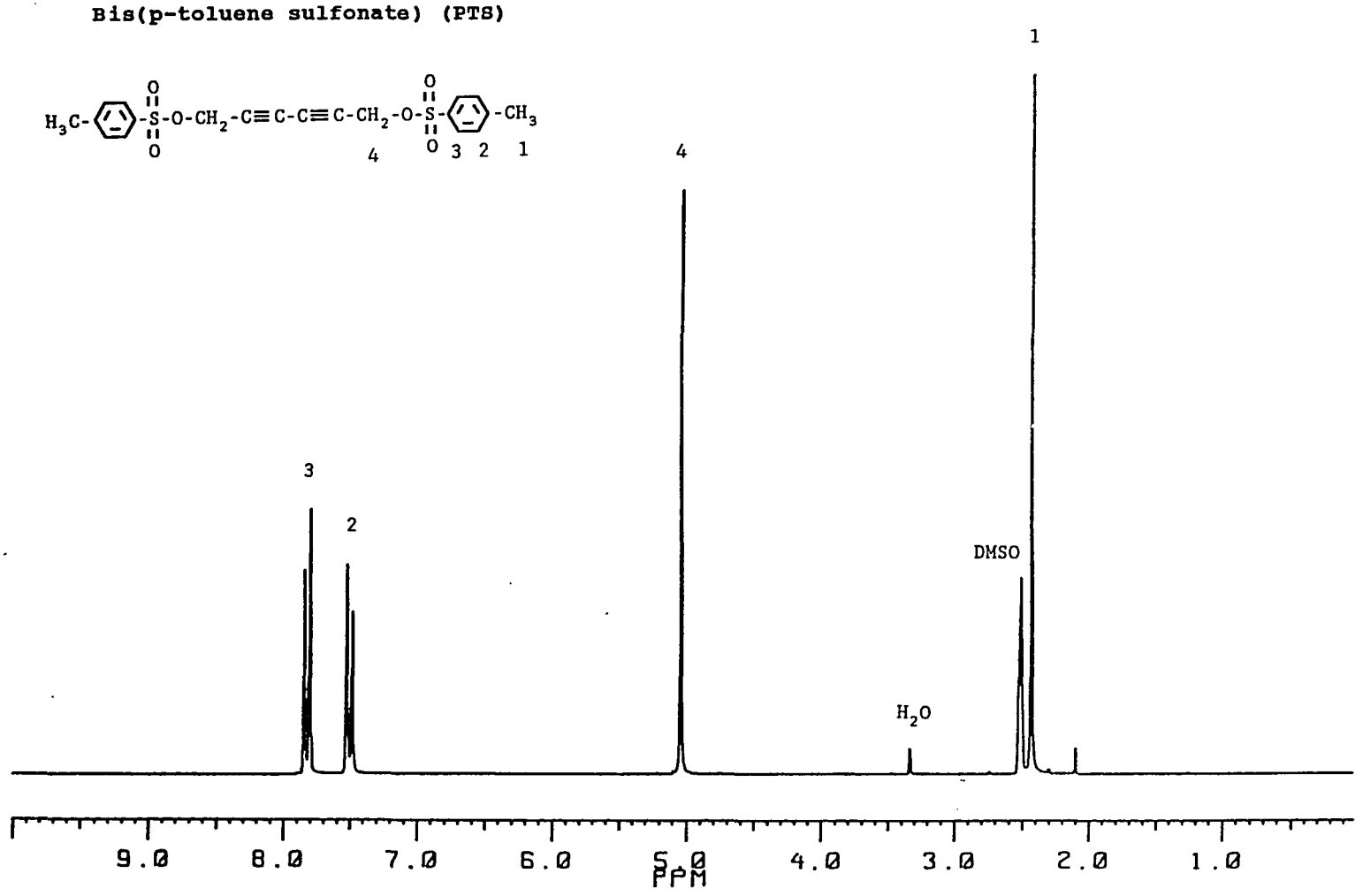


Fig. 4-6 ^{1}H NMR spectrum of bis(p-toluene sulfonate) in DMSO

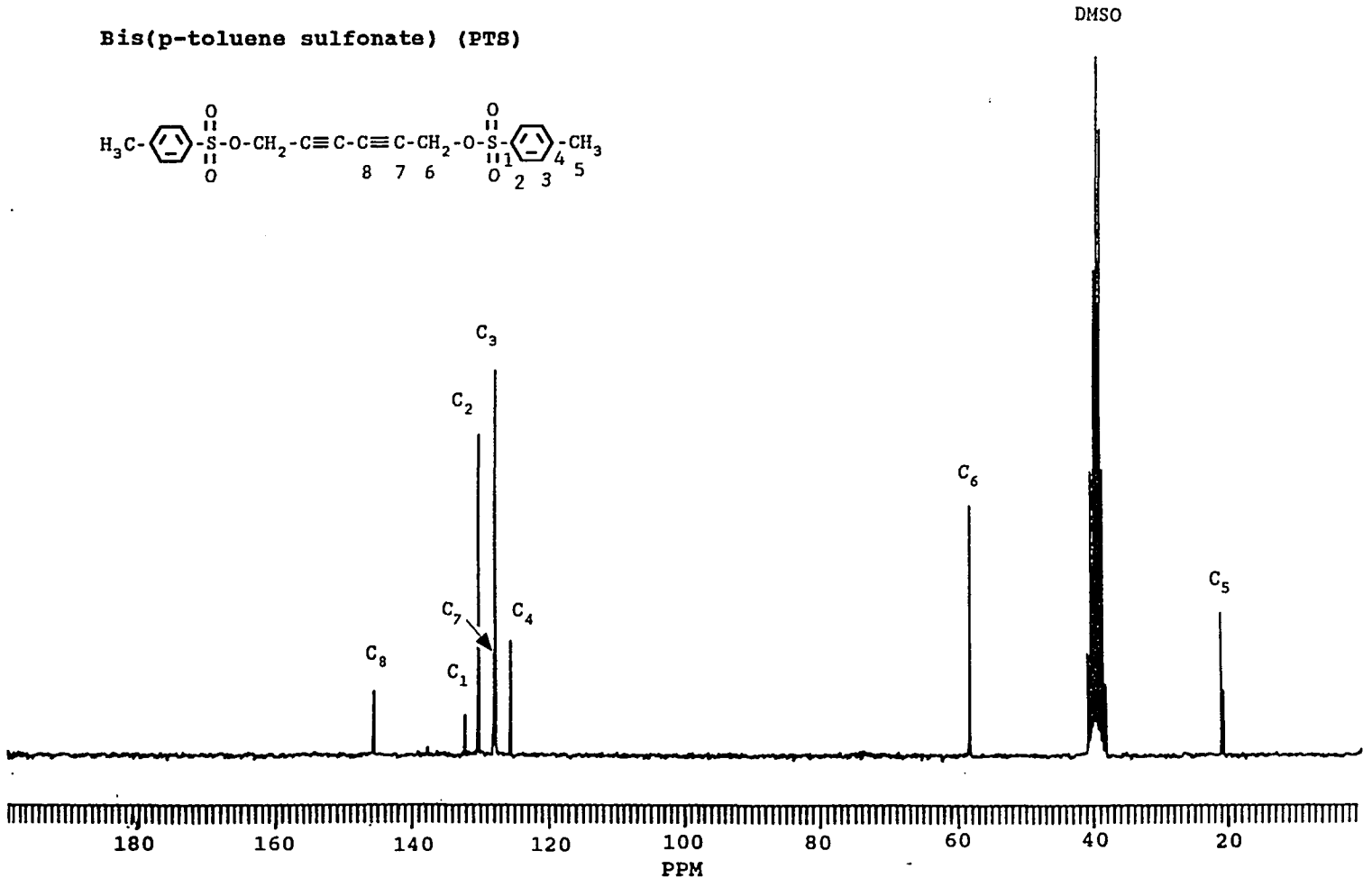


Fig. 4-7 ^{13}C NMR spectrum of bis(p-toluene sulfonate) in DMSO

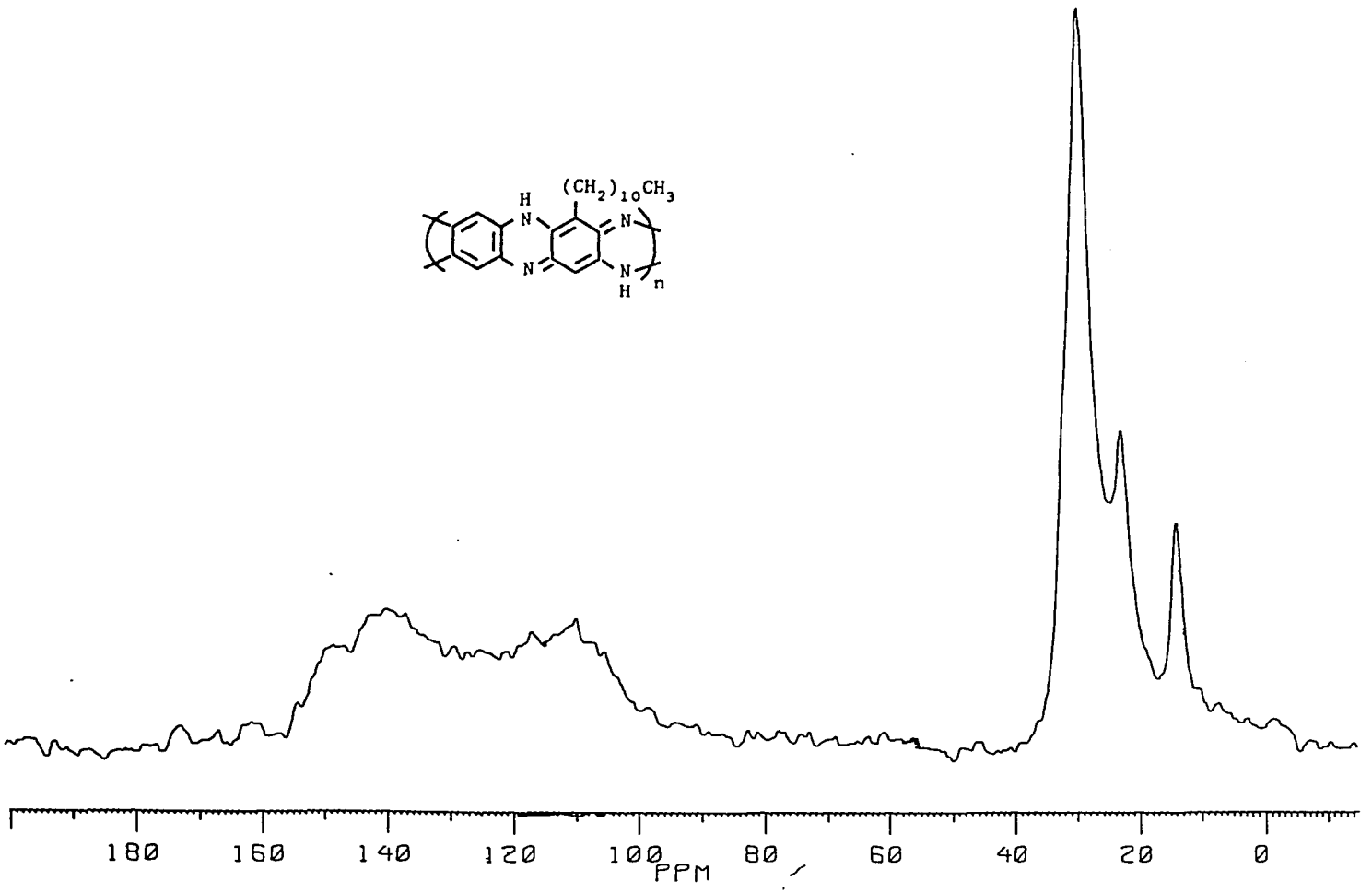


Fig. 4-8 Solid state ^{13}C NMR spectrum of ladder polymer

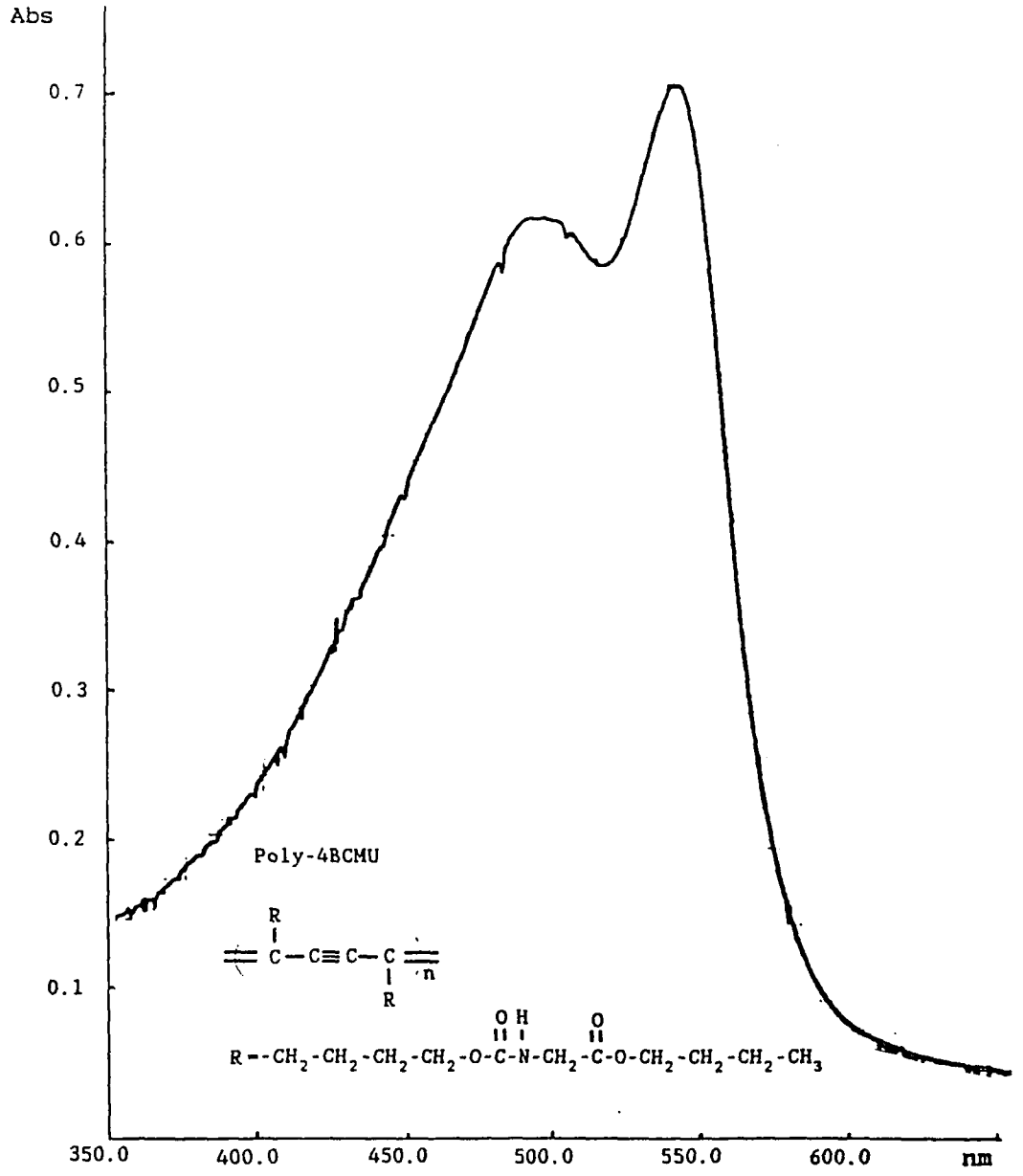


Fig. 4-9 UV spectrum of poly-4BCMU

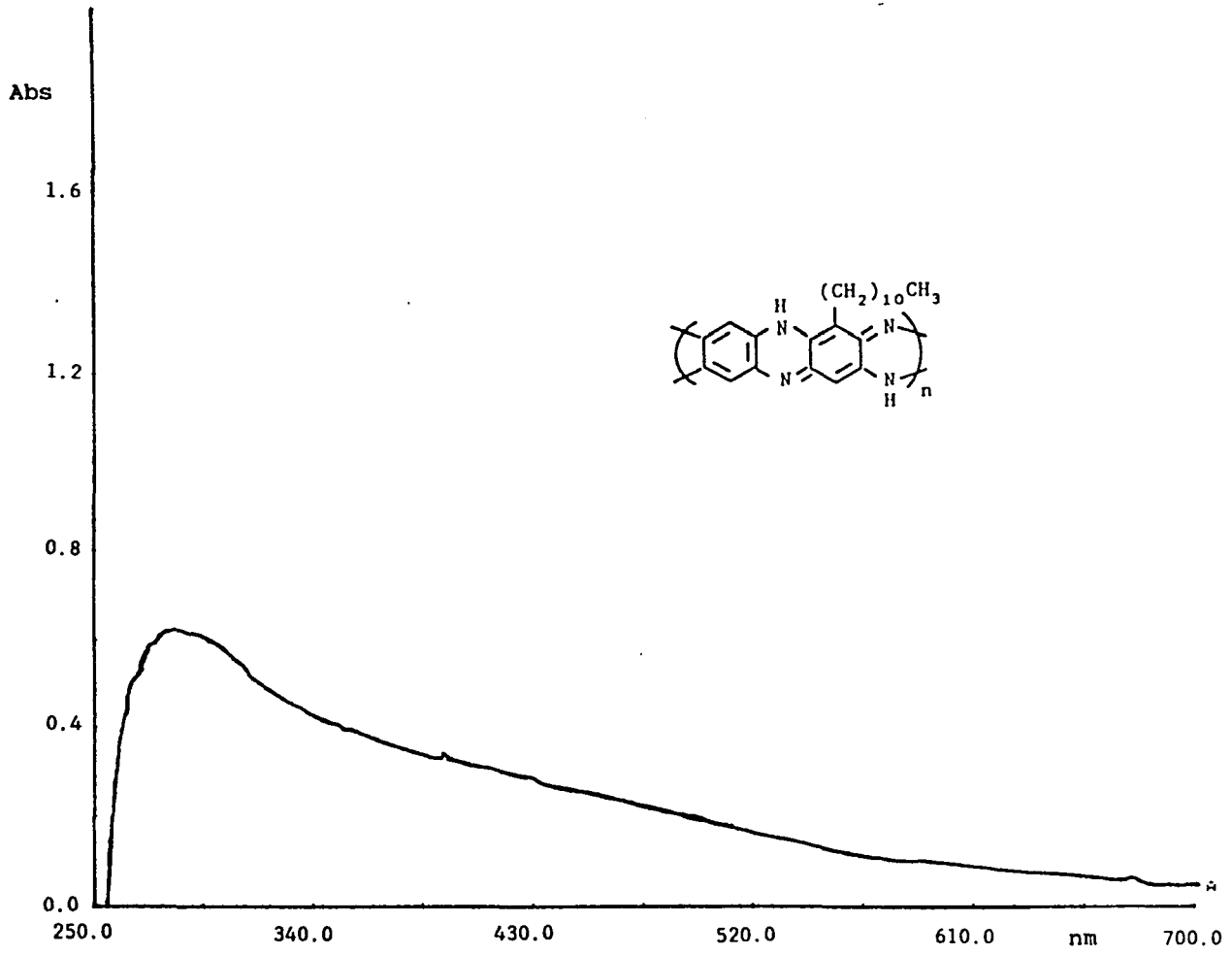


Fig. 4-10 UV spectrum of ladder polymer

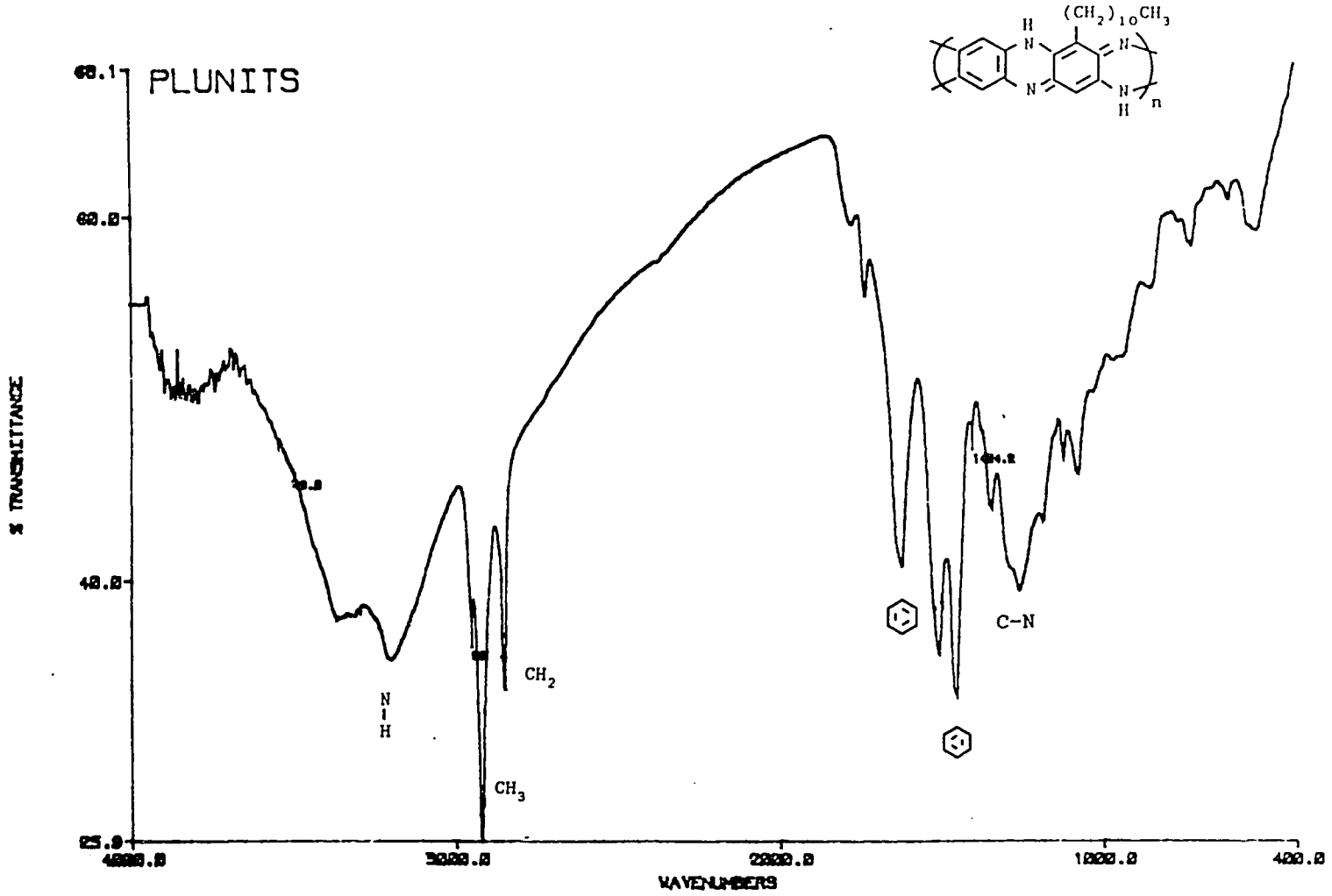


Fig. 4-11 FT-IR spectrum of ladder polymer

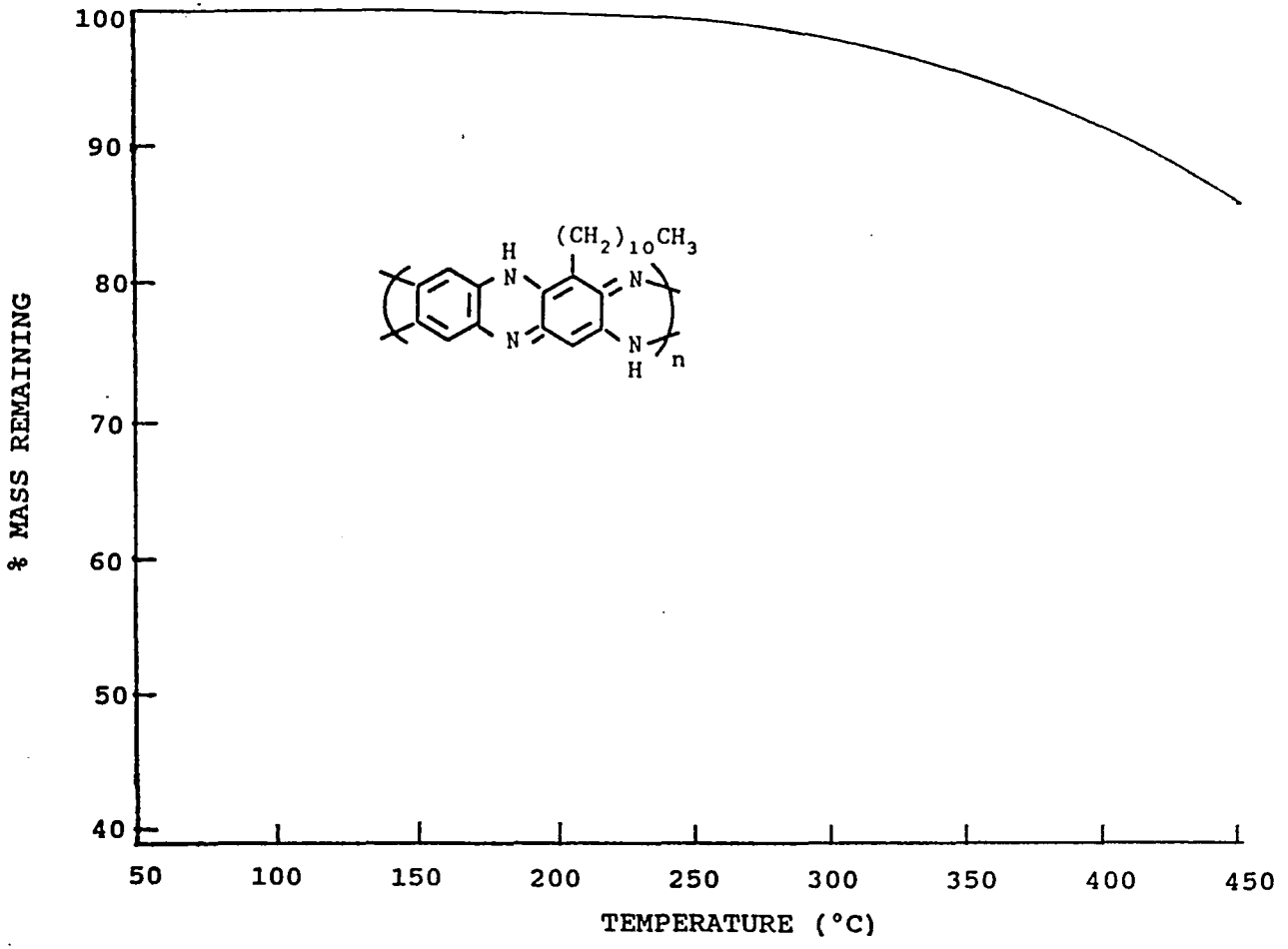
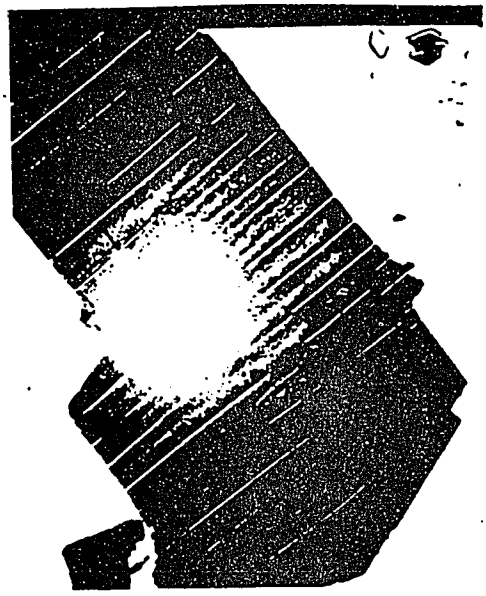


Fig. 4-12 TGA thermogram of ladder polymer

(a) X40, polarized at 90°



(b) X100, polarized at 90°

Fig. 4-13 Photomicrographs of poly-PTS single crystals

4.3.6. Ultrafast Nonlinear Optical Processes of Poly-4BCMU In PMMA Matrix Films[24]

The results on the third order optical nonlinearities and response times of poly-4BCMU in PMMA matrix films measured using optical phase conjugation and picosecond and femtosecond optical Kerr effect are shown in Table 4-2:

Table 4-2. third order optical nonlinearities and response times (τ) in poly-4BCMU in PMMA matrices films.

substance	λ (μm)	$\chi^{(3)}(10x^{-13}esu)$	τ (ps)
poly-4BCMU film	0.62 (NR)*	320	<1
	0.53 (R)**	3200	12

* NR — denotes non-resonance process.
**R——denotes resonance process.

The resonant $\chi^{(3)}$ of poly-4BCMU in PMMA matrices film is about $3x10^{-10}$ esu with a subpicosecond π-electron and a ~12 ps response time which is about 30 times smaller than the resonant $\chi^{(3)}$ obtained from crystalline polydiacetylenes.[31,32] This result is expected. Crystalline polydiacetylenes offer a larger $\chi^{(3)}$, while polymer films offer convenience and flexibility. The non-resonant $\chi^{(3)}$ of poly-4BCMU in PMMA matrices film was found to be ~10 times smaller than the resonant $\chi^{(3)}$ with a faster than 1 ps response time due to the π-electron cloud distortion is about ten times smaller than the value of

resonant $\chi^{(3)}$.

4.3.7. Intensity Dependence of Picosecond Nonlinear Response Time of Poly-4BCMU in PMMA Matrix Films[25]

The slow relaxation component of poly-4BCMU in PMMA matrices red films in time resolved DFWM measurements was found to be intensity dependent.[25] The reason is unknown. However, under intense light irradiation, the poly-4BCMU in PMMA matrices red films most likely experienced a transient reversible structural change originating from the side chain intramolecular hydrogen bonding. This is verified by the time resolved DFWM measurement on the yellow form films. The yellow films were obtained through exposing red films to the vapor of trifluoroacetic acid, a hydrogen bond breaking agent. The yellow films could be converted back to the original red films by evacuation under vacuum, clearly indicating that the only difference between the two forms is the extent of side group hydrogen bonding. Experimental results in the yellow form did not show the intensity dependent for slow component as observed in the red form of poly-4BCMU in PMMA matrices films. Furthermore, the optical absorption spectra of the red film were measured before and after the intense laser pules excitation. No difference was observed between two spectra, indicating that the structure change in the poly-4BCMU films is reversible.

4.4. Conclusions

Soluble poly-4BCMU was synthesized using novel

synthetic routes developed by Patel. Poly-4BCMU in PMMA matrix films with high optical transparency and about 0.7 absorption at 530 and 620 nm were prepared in a large crystallization dish with controlled vapor pressure of the methylene chloride solvent. The third order optical nonlinearities and response times of poly-4BCMU in PMMA matrix films have been measured using picosecond and femtosecond optical Kerr effect and phase conjugation. The resonant $\chi^{(3)}$ of poly-4BCMU in PMMA matrix film was found to be about $3x10^{-10}$ esu with a subpicosecond (~12 ps) response time. The non-resonant $\chi^{(3)}$ term was found to be $3x10^{-11}$esu (~10 times smaller than the resonant $\chi^{(3)}$) with a faster than 1 ps response time.

The relaxation time of the transient degenerate four-wave mixing grating in poly-4BCMU in PMMA matrix films has been found to be laser energy fluence dependent. This phenomenon is attributed to a transient reversible light induced structure change in poly-4BCMU films, involving a cooperative effect originating from side-chain intramolecular hydrogen bonding.

Approximately 4x7 millimeter in area and about one micrometer in thickness of thin film single crystals of poly-PTS was prepared using solution-shear growth method, but some defects was found on the surface of this crystal due to the problem of the speed control and pressure of solution-shear apparatus.

A soluble ladder polymer was synthesized, but was not suitably for used in nonlinear optical study due to its

dark color and high light absorption.

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CHAPTER IV. SYNTHESIS AND CHARACTERIZATION OF π-ELECTRON CONJUGATED POLYMERS AND THEIR NONLINEAR OPTICAL PROPERTIES

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