

**Isodisperse Telechelic Polymers and their Polyurethane Derivatives
Sample Preparation**

Final Technical Report

by

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Abstract

This report describes the preparation of six hydroxy-terminated polybutadiene (HTPBD) samples and their hydrogenated (polyethylene) derivatives (HTPE). The polybutadiene samples, with nominal average molecular weights M_n of 1000, 1500, 2000, 3000, 5000, and 10000, have been prepared using the so-called "isodisperse telechelic polymerization" method under non-isothermal conditions. The HTPBD samples produced were characterized by gel permeation chromatography, FT-IR and $^1\text{H-NMR}$ and showed a narrow polydispersity approaching the theoretical limit. From the HTPBD samples isodisperse HTPE samples were prepared by hydrogenation under heterogeneous conditions, using a freshly prepared 30% palladium/charcoal catalyst. Between July 1995 and May 1997, 100-g batches of the twelve samples thus prepared were sent to the US army research laboratory for further experiments.

Keywords: isodisperse telechelic polymerization, hydroxy-terminated polybutadienes, hydroxy-terminated polyethylenes, non-isothermal polymerization, hydrogenation

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Introduction

In the past decade there has been a great interest in hydroxy telechelic polymers with designed low molecular weights and narrow polydispersity. There may be several applications for this type of polymers:

- ◆ Incorporation into a polymeric matrix to alter its physical properties such as viscosity.
- ◆ Chemical modification of the reactive sites: the hydroxy end groups can be converted into acrylic, acid or acid chloride groups.
- ◆ Crosslinking with multifunctional reagents to obtain macromolecular networks.

Free-radical polymerization is probably the most cost-effective for preparing such polymers with functional groups in the α,ω positions [2, 3]. In that case the functionality is determined by the nature of the initiating radicals. However, controlling polydispersity has often been a problem in free-radical polymerizations. This is mainly related to changing conditions during the polymerization reaction: decreasing concentrations of initiator and monomer, and increasing viscosity. At the Research Group of Macromolecular Chemistry of the Hungarian Academy of Sciences, a method was developed to counteract these effects and produce polymers with minimal polydispersity P_w/P_n [4]. In theory, in the case of recombination, the polydispersity P.D. equals 1.5 and the functionality F of the polymer equals 2.

The US Army Research Laboratory is interested in obtaining elastomers with optimal physico-chemical properties. Isodisperse telechelic polymers such as HTPBD or HTPE could constitute such materials according to the theory of elasticity. This report describes the synthesis and chromatographic/spectroscopic characterization of six HTPBD samples with nominal average molecular weights M_n of 1000, 1500, 2000, 3000, 5000, and 10000. The optimization of the reaction conditions and the development of the corresponding temperature programs has been described in detail in our previous report "Isodisperse Telechelic Polymers and their Polyurethane Derivatives" (contract # N68171-95-C-9068) [1]. Six HTPE samples were then prepared from their HTPBD precursors through hydrogenation using a palladium/charcoal catalyst. The twelve samples were sent to the US Army Research Laboratory in 100-g amounts for further characterization.

Experimental

Chemicals

4,4'-azo bis-4-cyano-*n*-pentanol (ACP) synthesized in our own laboratory from 5-hydroxy-2-pentanone (Fluka); molecular weight: 252; melting point: 81-83 °C or 94-96°C (two isomers). Hydrogen peroxide, 50% solution by weight, from Peroxid Chemie GmbH, Germany. 1,3-butadiene, purity > 99% from Matheson.

Polymerization

The polymerization reactions were carried out in an acid-proof autoclave from Parr (net volume 900 ml; maximum pressure 190 bar). The reactor can be stirred mechanically, electrical heating and cooling with circulating water can be applied from the outside. After addition of all solvents and dissolution of the initiator the reactor is flushed with pure nitrogen and evacuated several times. Then the monomer (preheated to 30°C) is added in liquid form from a buffer vessel and the polymerization reaction is started according to a specific temperature program.

Purification

After the polymerization reaction the pressure is released and the unreacted monomer is condensed and recovered. The recombination product from initiator and hydrogen peroxide is removed by washing with distilled water in a separation funnel. The remaining peroxide is reduced to below 1 ppm level by passing through a zeolite column activated with cobalt ion. The solvents are removed in a film evaporator by nitrogen heated to 140°C [1].

Hydrogenation

3 g of freshly prepared 30% Pd/C catalyst and 30 ml of *n*-hexane was placed in a Parr hydrogenation apparatus. After repeated flushing/evacuation with nitrogen and then with hydrogen the catalyst was hydrogenated for 20 minutes at 60°C and 4 bar. Then 10 g of the HTPBD sample was added in 370 ml of *n*-hexane and was hydrogenated at 60°C and 4 bar during 1 hour. After filtration over a glass filter the catalyst was washed and the solvent was evaporated under vacuum. Eleven batches were prepared and combined to yield the amount required. Heating to 100°C under reduced pressure served to remove the last traces of solvent. See also ref. [5].

Instrumental Analysis

Proton NMR spectra were recorded using a Varian 400 instrument. Fourier transform infrared spectra (FT-IR) were recorded using a Bomem MB-100 spectrophotometer. The molecular weight distribution was determined by means of gel permeation chromatography (GPC) using a setup from Waters: pump model 510, injector model U6K and a set of four columns packed with crosslinked polystyrene gel ("ultrastyrigel") of particle size less than 10 microns and pore sizes of 10 µm, 1 µm, 100 nm and 50 nm.

The functionality of the polymers was calculated from the hydroxy-endgroup concentration and the molecular weight of the polymers, as described in our previous report [1]. The apolar solvent used (cyclohexane) precludes any interference from the ACP initiator recombination product, as it is insoluble in this solvent.

Preparation of HTPBD Samples

Polybutadiene samples were synthesized with nominal average molecular weights M_n of 1000, 1500, 2000, 3000, 5000, and 10000. The polymerization conditions applied are listed in Table 1. The details of the non-isothermal temperature programs have been described earlier [1].

Table 1: Polymerization conditions and reagents used.

Samples	Monomer mol/l	Solvent (ml)		Initiator (mol/l)		Polym. time (min)	Temp. °C
		sec. butanol	dioxane	ACP	H ₂ O ₂		
HTPBD-1000	6.0	200	200	0.145	-	175	73-96
HTPBD-1500	6.0	200	200	0.145	-	500	65-96
HTPBD-2000	6.0	400	-	2.14E-02	0.63	180	80-96
HTPBD-3000	6.0	400	-	2.14E-02	0.53	360	75-96
HTPBD-5000	6.0	400	-	5.73E-03	0.18	480	70-96
HTPBD-10000	6.0	200	200	8.00E-04	6.15E-03	720	70-96

The functionality of the HTPBD samples was determined and was found to be close to the theoretical value of 2 for all samples (see Table 2). The conversion rates of the polymerization reactions varied between 20 and 40% for most samples, but was only 10% for the HTPBD-10000 sample (see Table 2). The experimentally determined average molecular weights and polydispersity data (as measured by GPC) are also listed in Table 2 and visualized in Figure 1.

Table 2: Functionality, conversion rates and polydispersity of HTPBD samples

Samples	Functionality	Conversion %	GPC results	
			M_n	M_w/M_n
HTPBD-1000	1.62	30.0	1245	1.34
HTPBD-1500	2.10	33.0	1552	1.34
HTPBD-2000	1.90	20.0	1870	1.62
HTPBD-3000	2.44	40.0	3250	1.98
HTPBD-5000	1.98	25.0	5230	1.72
HTPBD-10000	1.97	10.0	10800	1.95

As shown in Table 2, the molecular weight distribution of the samples HTPBD-1000 and HTPBD-1500 is very low, even below the theoretical value of 1.5. These low polydispersities can be expected to have a very positive effect on the elastic properties of the resulting polyurethane materials according to the elasticity theory.

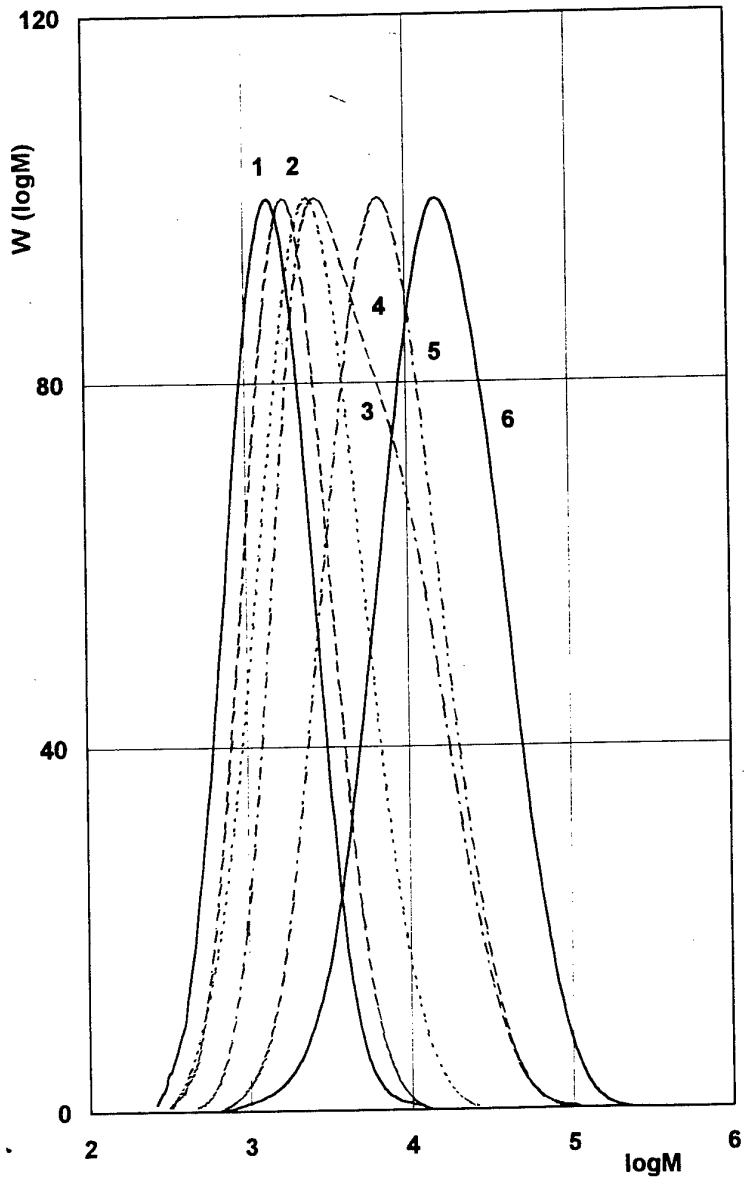


Figure 1: Molecular weight distribution of the HTPBD samples, as determined by GPC. 1= HTPBD-1000; 2= HTPBD-1500; 3= HTPBD-2000; 4= HTPBD-3000; 5= HTPBD-5000; 6= HTPBD-10000.

The microstructure of the HTPBD samples was investigated using FT-IR and ¹H-NMR spectroscopy; the spectra can be found in Annex 1. The FT-IR spectra show only a few differences between the samples. Obviously the broad OH-stretch absorption at 3200-3600 cm⁻¹ (hydroxy endgroups) is relatively strong for the short oligomers and practically invisible for the HTPBD-5000 and HTPBD-10000 samples. For the same reason the cyanide stretch vibration (initiator fragments) is most strongly observed in the spectra of the shortest oligomers.

During the course of the polymerization three different configurations can be formed: 1,4-trans, 1,2- and 1,4-cis linkages. The distribution of these linkages was determined based on the ratios of a number of out-of-plane IR vibrational absorptions, as described in our previous report [1]. The ratio between the number of 1,2-linkages and 1,4-linkages was also determined by proton NMR spectroscopy; the two configurations can be distinguished based on the unsaturated proton intensities at 4.9-5.0 and 5.2-5.4 ppm, respectively [1]. In general, the results of the two techniques agree quite well, although in general the percentage of 1,2-linkages appears to be a little higher according to the NMR results in comparison to the FT-IR results (see Table 3). In general, the ratio of 1,2-linkages vs. 1,4-linkages is about 1 to 5 in all samples, irrespective of the average chain length.

Table 3: Microstructure of HTPBD samples based on FT-IR and NMR results (%).

Samples	FT-IR			proton NMR	
	1,2 link	1,4 link <i>cis</i>	1,4 link <i>trans</i>	1,2 link	1,4 link
HTPBD-1000	11	54	35	15	85
HTPBD-1500	11	58	31	15	85
HTPBD-2000	13	54	33	17	83
HTPBD-3000	13	53	34	18	82
HTPBD-5000	13	54	33	17	83
HTPBD-10000	13	59	28	14	86

Preparation of HTPE Samples

Before the hydrogenation, new batches of HTPBD were prepared, using approximately the same conditions as those employed for the first set of HTPBD samples. The resulting products were analyzed by GPC, FT-IR and proton NMR, and the OH-functionality was also determined. Again the resulting polydispersities were quite narrow ($1.5 < 2$) and again the polydispersity was smallest in the case of samples HTPBD-1000 and HTPBD-1500 (see Table 4). Using the same method as described above, FT-IR and proton NMR spectroscopy was employed to determine the distribution of 1,2-linked *vs.* 1,4-*trans* linked *vs.* 1,4-*cis* linked configurations of these precursor HTPBD polymers and the results were very similar to those obtained with the first batch (compare Table 3 and Table 5). Most of these structural investigations were carried out on the precursor HTPBD polymer rather than on the HTPE endproduct, as the solid nature of the polyethylene samples and their insolubility in most solvents would preclude such measurements of the endproduct, unless extremely powerful solvents such as trichlorobenzene and very high temperatures were used. Under the mild hydrogenation conditions applied in our laboratory the structural characteristics of the HTPBD chains (length, configuration of linkages) will remain unchanged and will therefore also describe the HTPE polymer samples. Of course the molecular weight of the oligomers will increase by 3.7 % due to the addition of two hydrogens per butadiene group.

Table 4: Functionality and polydispersity of precursor HTPBD samples used for the preparation of hydroxy-terminated polyethylene.

Samples	Functionality	GPC results	
		M_n	M_w/M_n
HTPBD-1000	1.98	1211	1.54
HTPBD-1500	2.03	1666	1.53
HTPBD-2000	2.01	2136	1.79
HTPBD-3000	2.05	3059	1.78
HTPBD-5000	1.97	5403	1.81
HTPBD-10000	1.99	10270	1.79

Table 5: Microstructure of precursor HTPBD samples based on FT-IR and NMR (%)

Samples	FT-IR			proton NMR	
	1,2 link	1,4 link <i>cis</i>	1,4 link <i>trans</i>	1,2 link	1,4 link
HTPBD-1000	11	54	35	17	83
HTPBD-1500	12	55	33	17	83
HTPBD-2000	11	55	34	17	83
HTPBD-3000	12	55	33	18	82
HTPBD-5000	12	54	34	17.5	82.5
HTPBD-10000	12	58	30	17.5	82.5

Hydrogenation of unsaturated polymers can, in principle, be accomplished in several ways. Several hydrogenation procedures were tested on small batches of polybutadiene polymer HTPBD-3000. Proton NMR was employed to determine the completeness of the reduction. Homogeneous catalysis with chloro-tris(triphenyl-phosphine)rhodium(I) was tested, and although the resulting product showed an almost complete reduction, the practical difficulties of removing catalyst traces from the product constituted a major drawback. Reductions under heterogeneous conditions with hydrazine hydrate as reducing agent and Raney-nickel or 10% Pd/C or PtO₂ as catalyst also failed. The best results were obtained using hydrogenated Pd/C in n-hexane. See the Experimental section and ref. [5] for further details on the hydrogenation experiments.

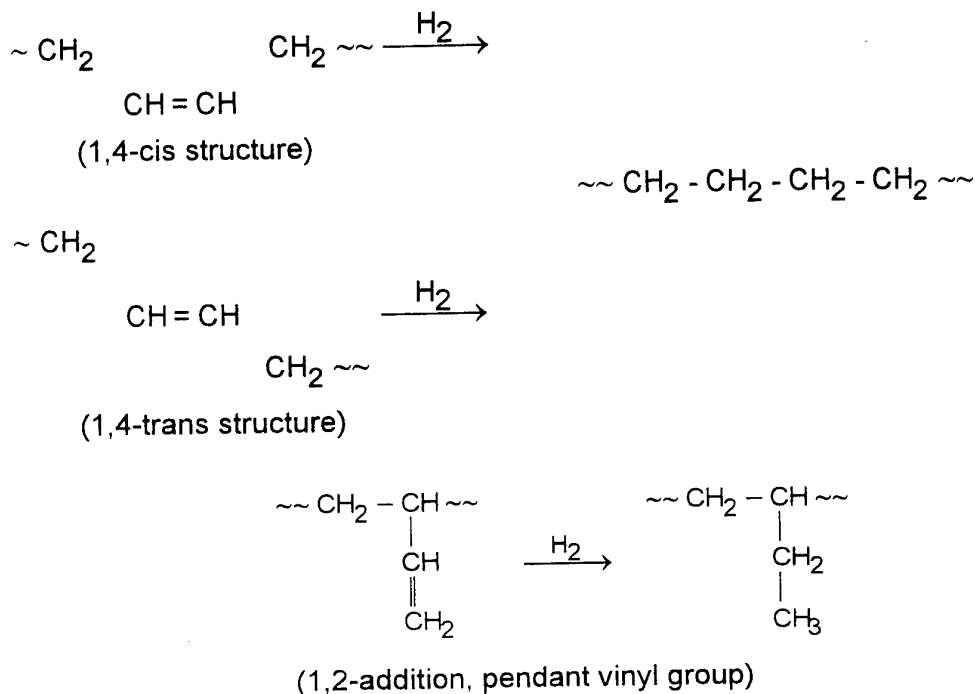


Fig. 2: Hydrogenation of 1,4-cis, 1,4-trans and 1,2 linked butadiene groups.

Figure 2 shows the structures resulting from hydrogenation of 1,4-linked and 1,2 linked polybutadienes. Given the mild hydrogenation conditions no structural changes or chain fission will occur. The hydrogenation of the above mentioned HTPBD samples led to the following products: HTPE-1000, HTPE-1500, HTPE-2000, HTPE-3000, HTPE-5000, HTPE-10000. These were analyzed by means of proton NMR before dispatching them to the US Army Research Laboratory (see Annex 2).

Conclusions

In a previous stage of this project the optimal conditions for non-isothermal radical polymerization were theoretically derived and the corresponding temperature programs were developed. This report describes the successful application of this approach to the synthesis of bifunctional polybutadiene polymers with a uniform chain length. Indeed for all samples a narrow polydispersity $M_w/M_n < 2$ was observed with gel permeation chromatography. The average molecular weights were usually well within 10-20 % of the target values.

From a second series of HTPBD samples showing similarly low polydispersity the corresponding saturated polyethylene derivatives were prepared by hydrogenation under heterogeneous catalytic conditions (Pd/C). One of the major advantages of this method is the easy separation and recovery of the catalyst.

This work has shown the potential of temperature-programmed radical polymerization for the production of polymers with uniform chain lengths. Application of these principles to the production of isodisperse copolymers has also been successful [6]. Such materials could ultimately be of great value for the production of cross-linked rubbers with excellent elastic properties.

Table 6: HTPBD and HTPE samples shipped to the US Army Research Laboratory

Samples	Shipping date	Mn
HTPBD-1000	Jan 25, 1996	1245
HTPBD-1500	Jan 25, 1996	1552
HTPBD-2000	Oct 13, 1995	1870
HTPBD-3000	July 6, 1995	3250
HTPBD-5000	Oct 13, 1995	5230
HTPBD-10000	Jan 25, 1996	10800
HTPE-1000	May 28, 1997	1256
HTPE-1500	May 28, 1997	1728
HTPE-2000	Feb 11, 1997	2215
HTPE-3000	March 7, 1997	3172
HTPE-5000	April 9, 1997	5603
HTPE-10000	April 9, 1997	10650

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- 5 F. Tüdös. Isodisperse Telechelic Polymers and their Polyurethane Derivatives. US Army contract # N68171-97-C-9002. 4th interim report (1997).
- 6 F. Tüdös. Isodisperse Telechelic Polymers and their Polyurethane Derivatives. US Army contract # N68171-97-C-9002. 5th interim report (1998).

ANNEX 1

CHARACTERIZATION OF HTPBD SAMPLES

- ◆ Molecular weight distribution of HTPBD-1000
- ◆ Molecular weight distribution of HTPBD-1500
- ◆ Molecular weight distribution of HTPBD-2000
- ◆ Molecular weight distribution of HTPBD-3000
- ◆ Molecular weight distribution of HTPBD-5000
- ◆ Molecular weight distribution of HTPBD-10000
- ◆ FT-IR spectra of HTPBD-2000, HTPBD-3000, and HTPBD-5000
- ◆ FT-IR spectra of HTPBD-10000, HTPBD-1500, and HTPBD-1000
- ◆ Proton-NMR spectrum of HTPBD-1000
- ◆ Proton-NMR spectrum of HTPBD-1500
- ◆ Proton-NMR spectrum of HTPBD-2000
- ◆ Proton-NMR spectrum of HTPBD-3000
- ◆ Proton-NMR spectrum of HTPBD-5000
- ◆ Proton-NMR spectrum of HTPBD-10000

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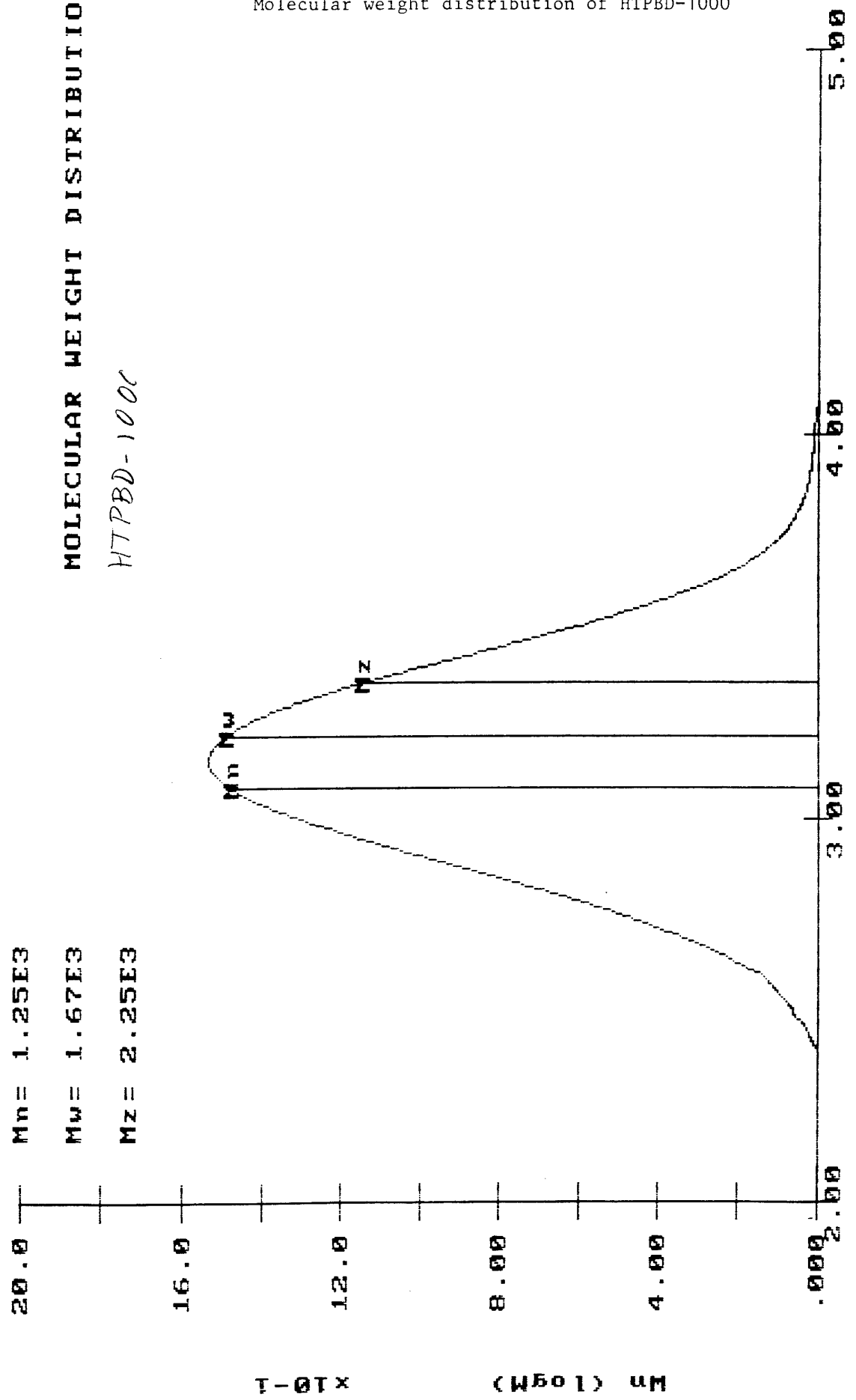
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MOLECULAR WEIGHT DISTRIBUTION

HTPBBD-1000

Molecular weight distribution of HTPBD-1000

Mn = 1.25E3
Mw = 1.67E3
Mz = 2.25E3



LOG M

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Mn = 1.53E3

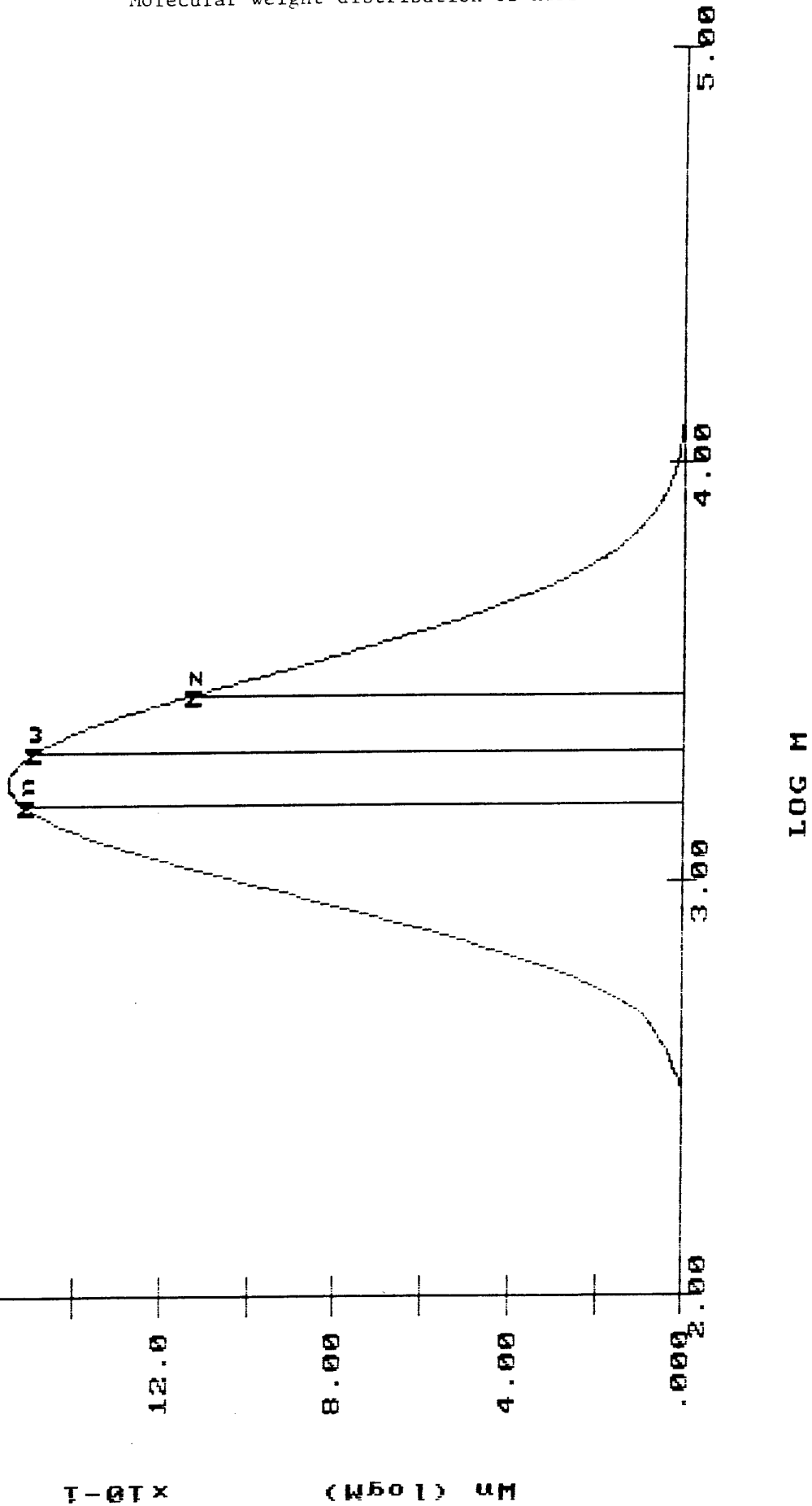
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Mz = 2.84E3

MOLECULAR WEIGHT DISTRIBUTION

HTPBD-1500

Molecular weight distribution of HTPBD-1500

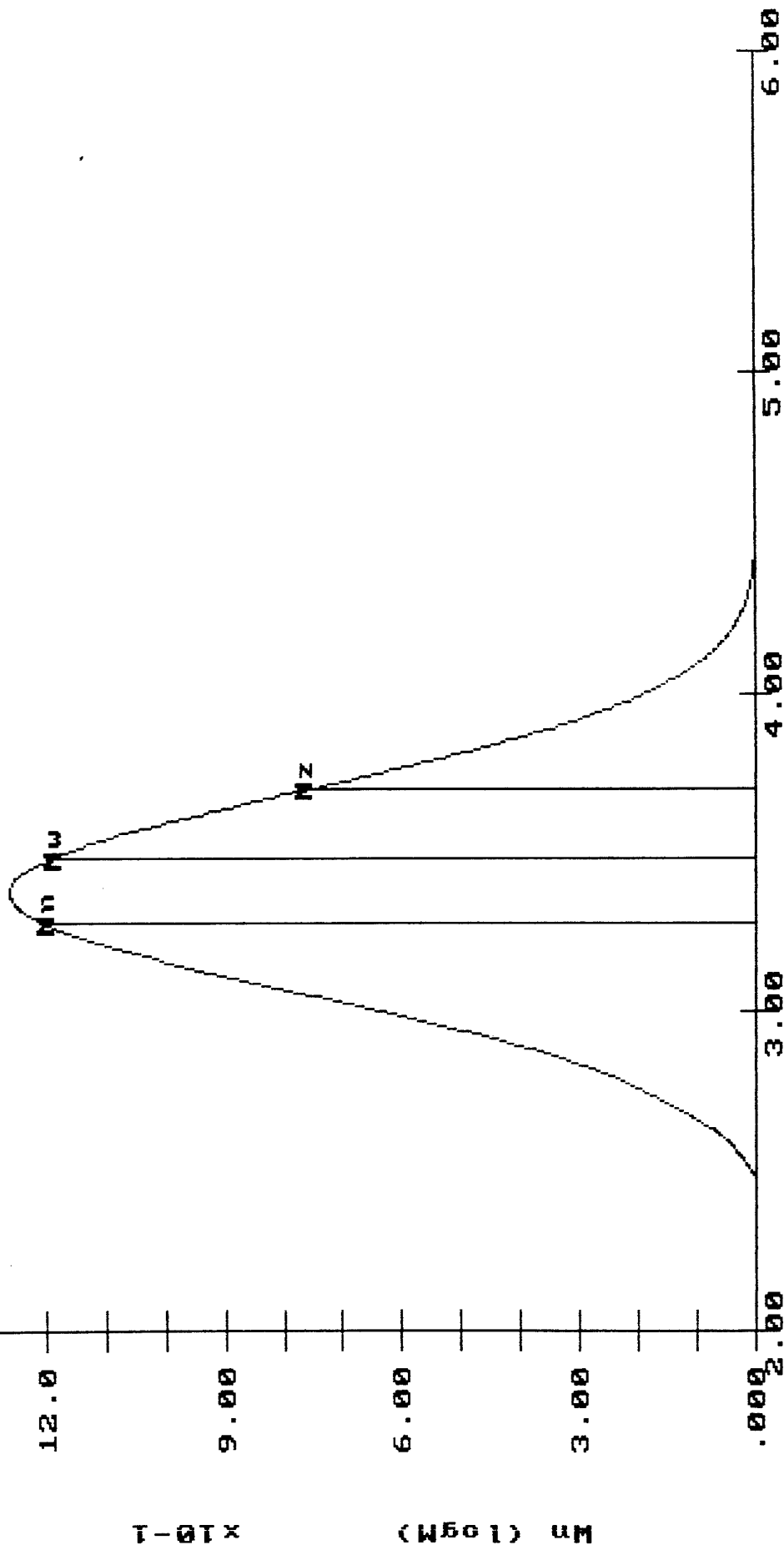


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Mn = 1.88E3
Mw = 3.03E3
Mz = 4.96E3

MOLECULAR WEIGHT DISTRIBUTION

HTPBD-2000



TINC M

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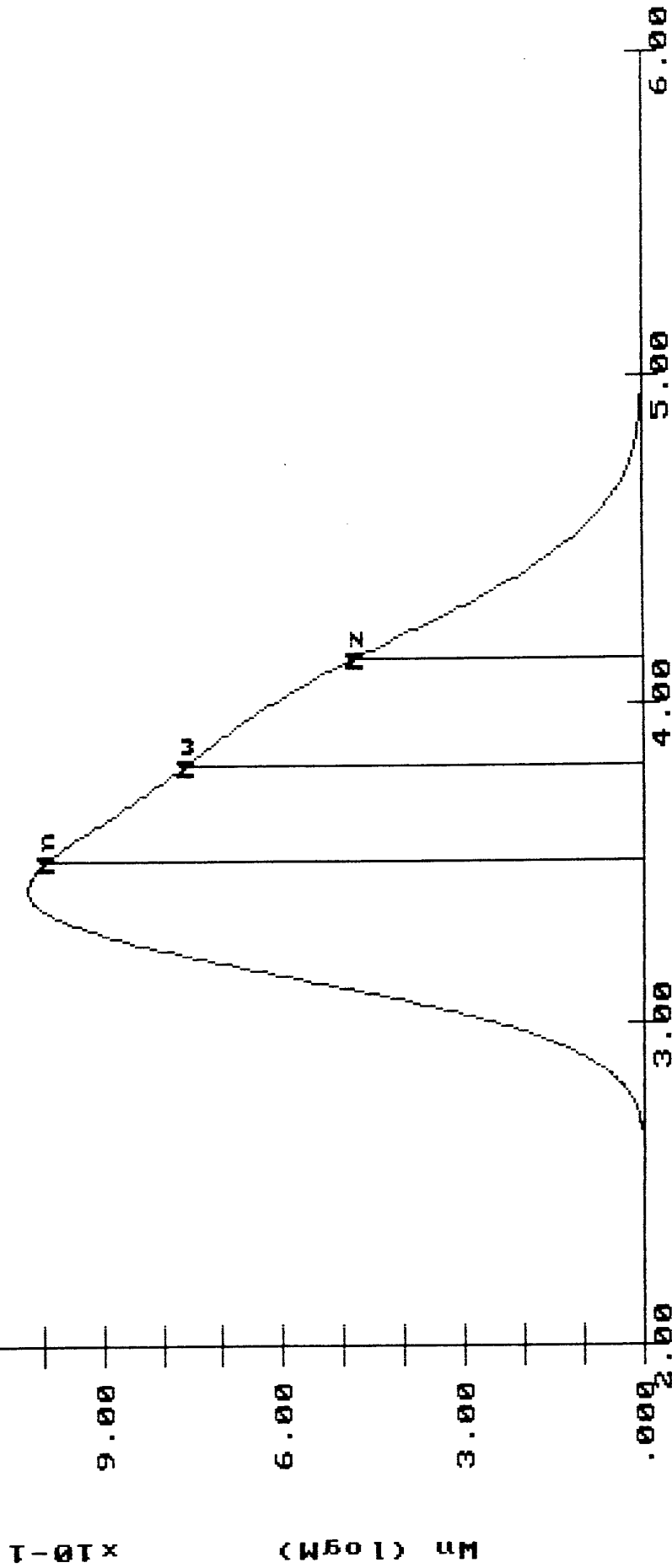
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Mw = 6.45E3

Mz = 1.38E4

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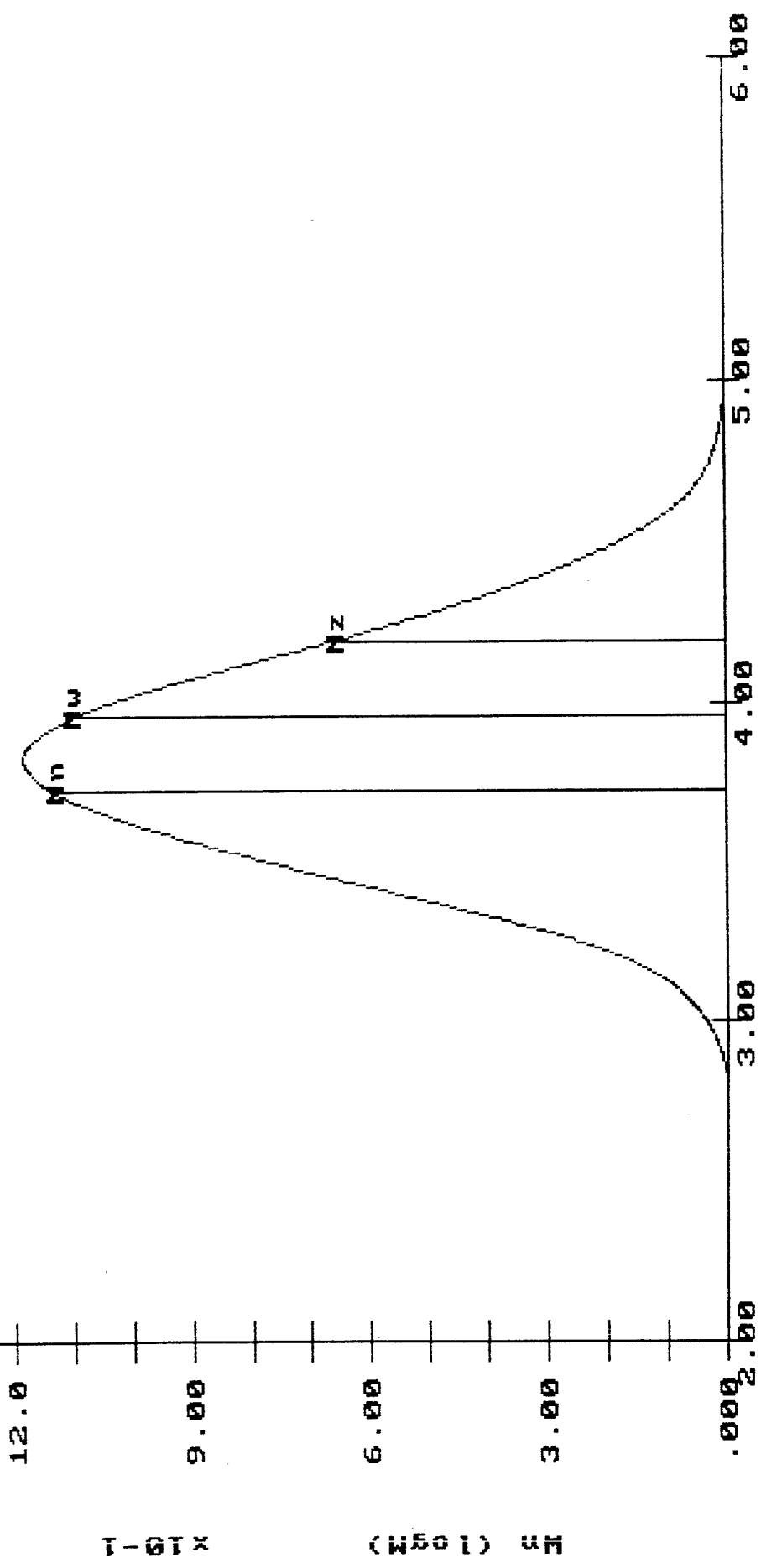
HT PBD - 3000



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Mw = 9.02E3
Mz = 1.57E4

MOLECULAR WEIGHT DISTRIBUTION
HT PBD-5000



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LOG M

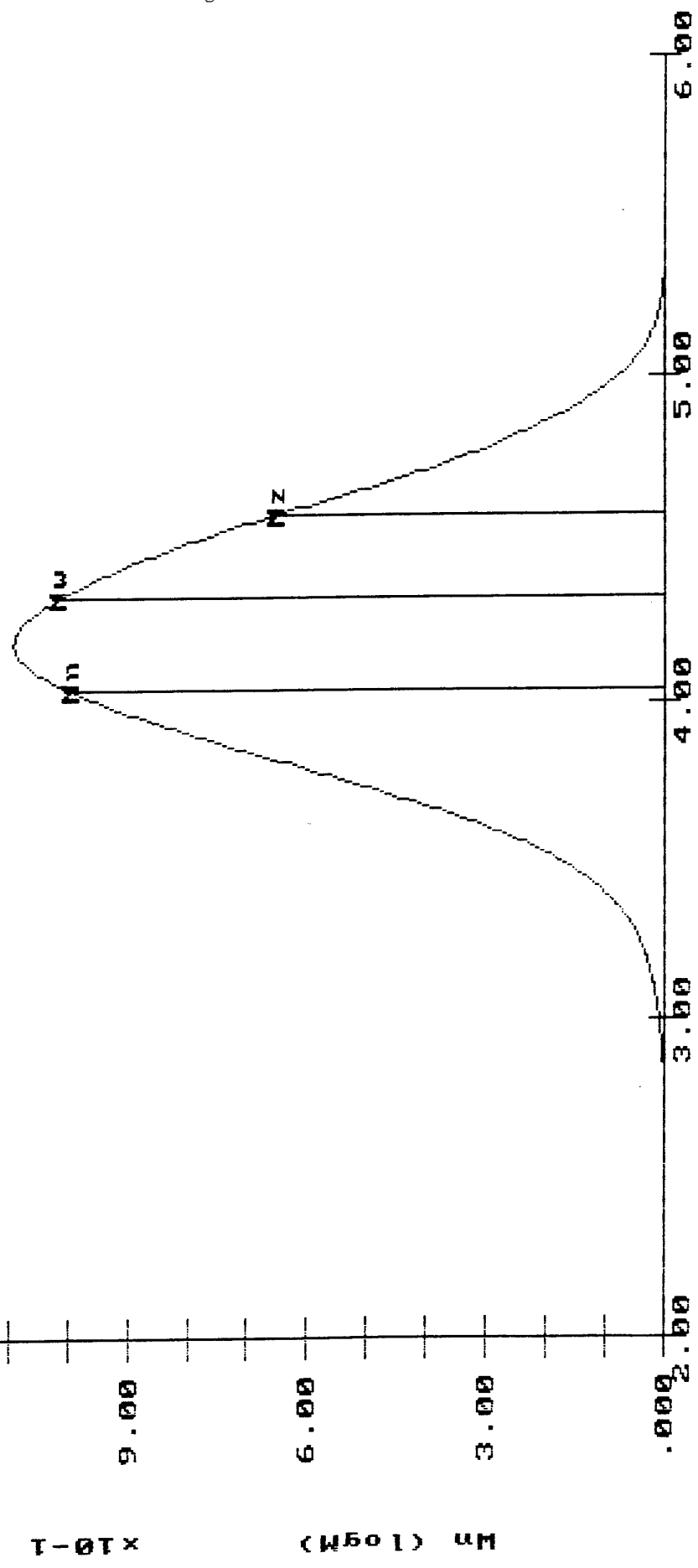
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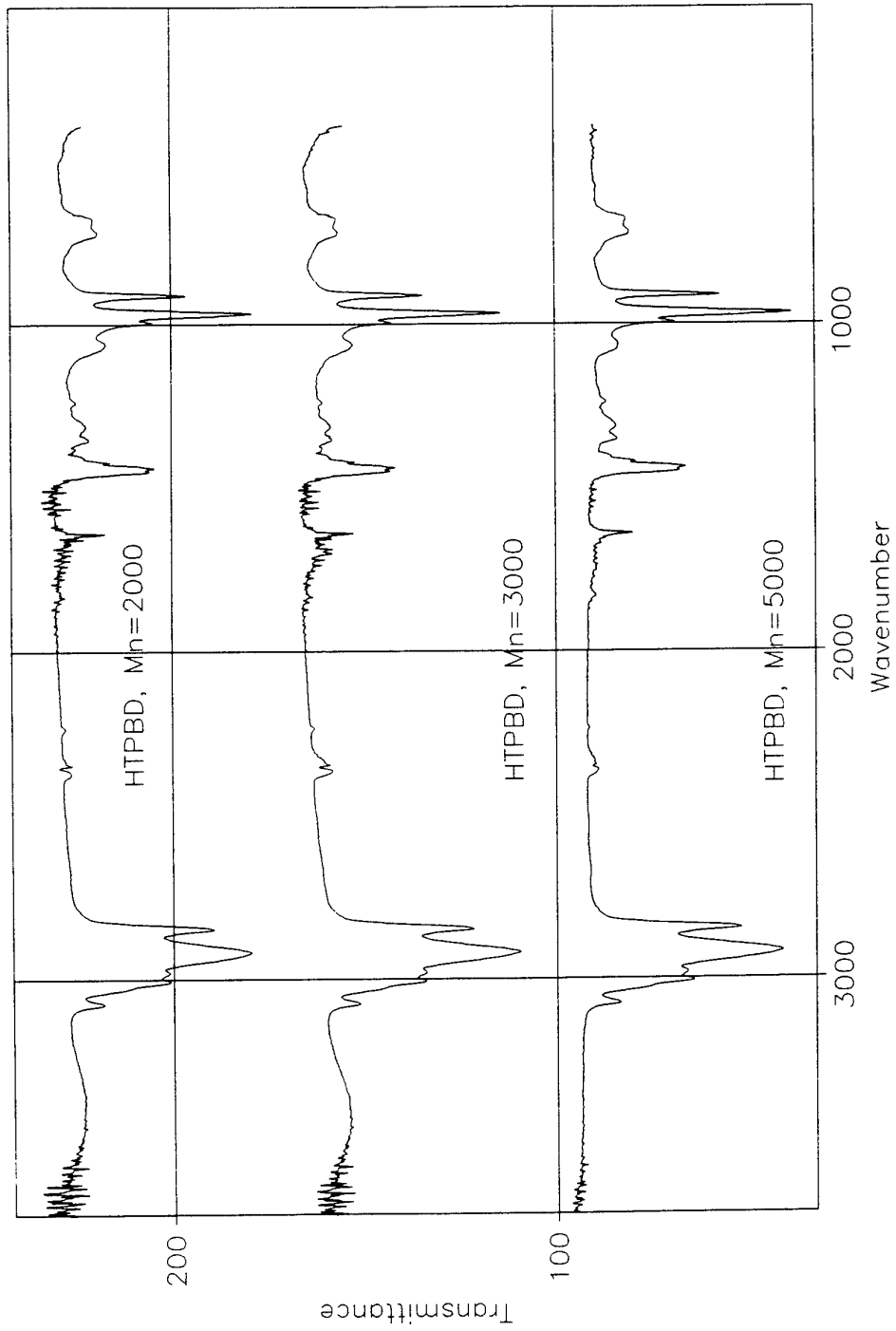
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Mz = 3.78E4

MOLECULAR WEIGHT DISTRIBUTION
HTPBD-10 000

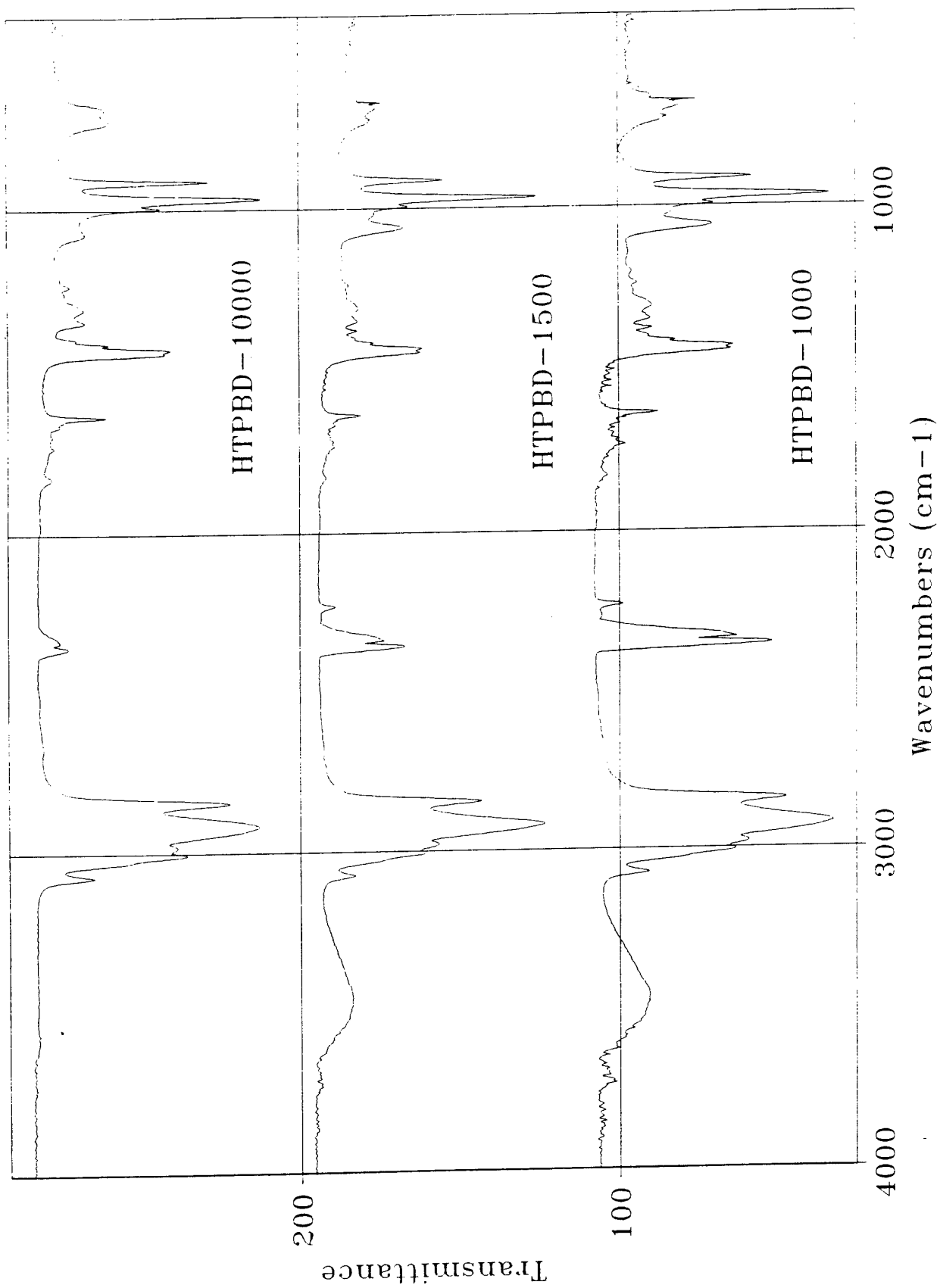
Molecular weight distribution of HTPBD-10000



LOG M



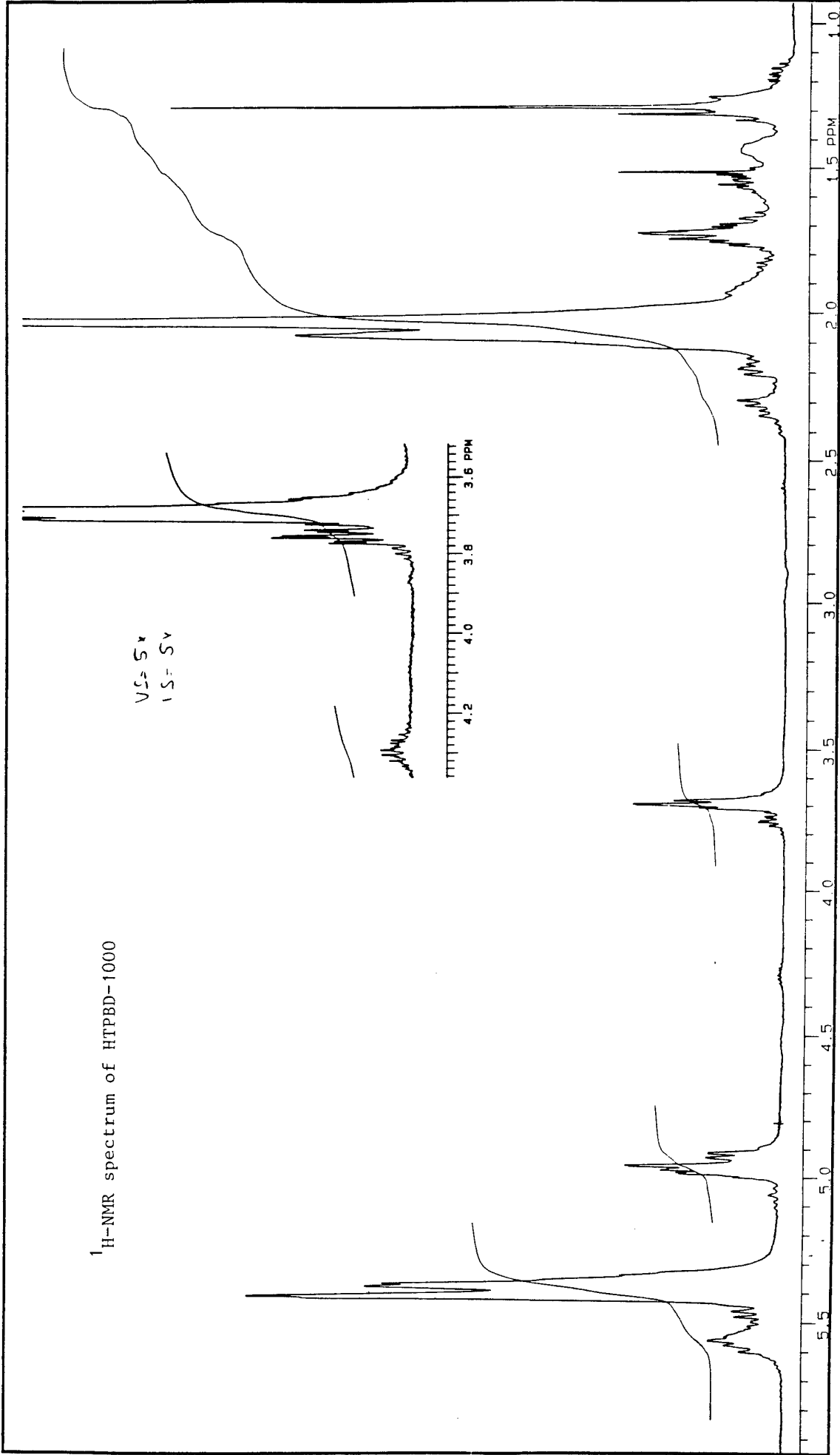
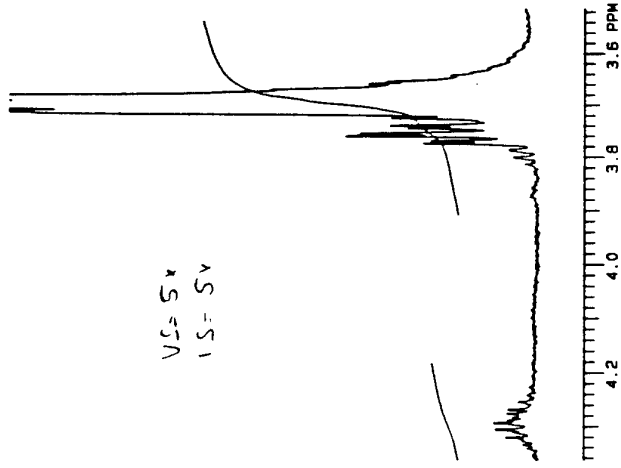
FT-IR spectra of polybutadiene diol samples.



FT-IR Spectra of HTPBD samples.

¹H-NMR spectrum of HTPBD-1000

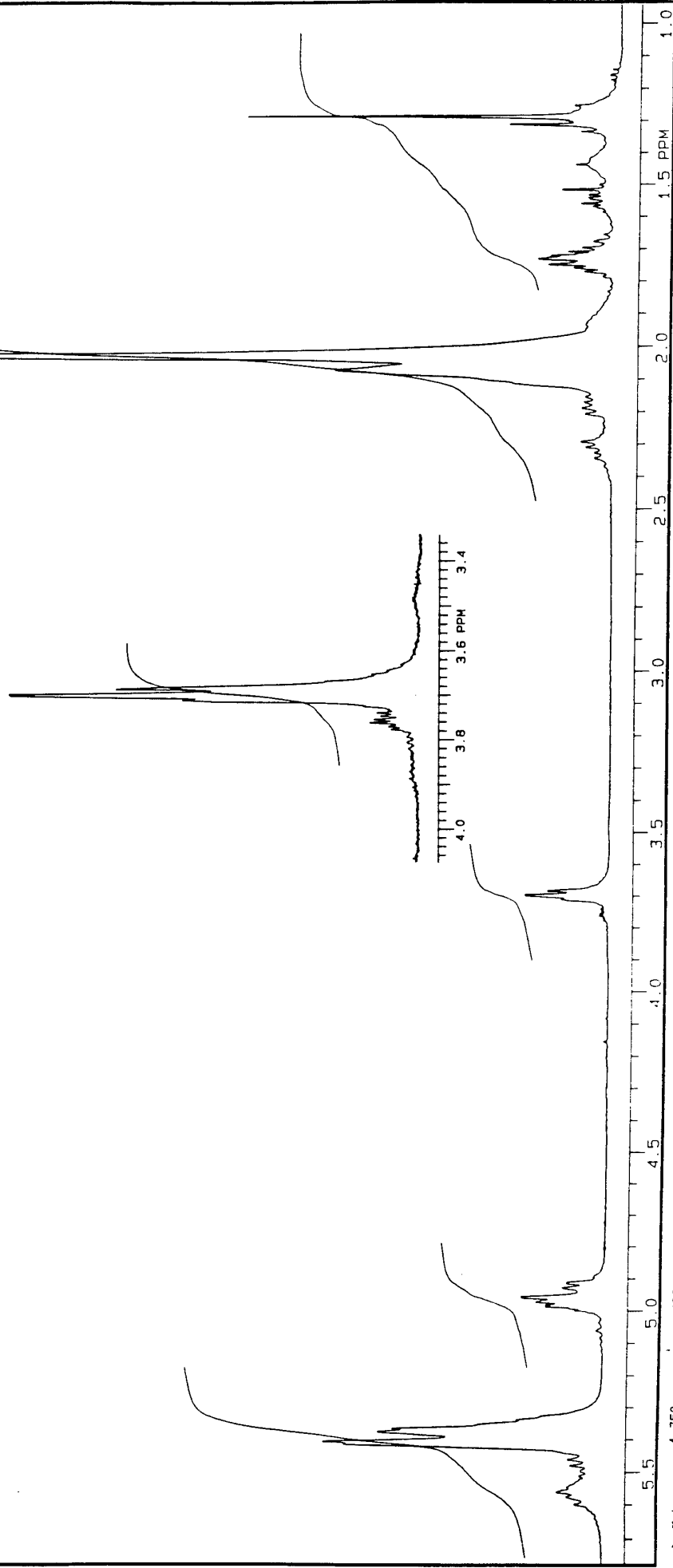
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IS= 5v



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Modulation Mode <u>C</u>		Pulse Width <u>---</u> sec		Reference <u>---</u>	
PLOT/PROCESSING					
FN <u>32</u> K RE		sec CD <u>---</u> sec		Pulse Sequence <u>STD1H</u>	
LB <u>---</u> Hz AF <u>---</u> sec CD <u>---</u>		Width <u>2005.1</u> Hz/ppm		Start <u>372.1</u> Hz/ppm	
EXPERIMENT					
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SAMPLE		H-8218 (19414)		130 (CDCL3)	
KESZLER B./E.O.		Date <u>05-01-96</u>		File <u>H</u>	
Number <u>---</u>		X <u>YXR</u>		400varian	

¹H-NMR spectrum of HTPBD-1500

US = 5 x
 IS = 5 x



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Nucleus 1.750 Offset 75.0 Hz
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 Modulation Mode C Freq 200 Hz
 Pulse Width 7.0 sec Power Mode -----

FN 32 K RE --- sec CD --- sec
 LB --- Hz AF --- sec CD --- sec
 Width 1933.1 Hz/ppm Start 376.7 Hz/ppm
 Reference -----

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 Temp --- °C
 Solvent CDCL3

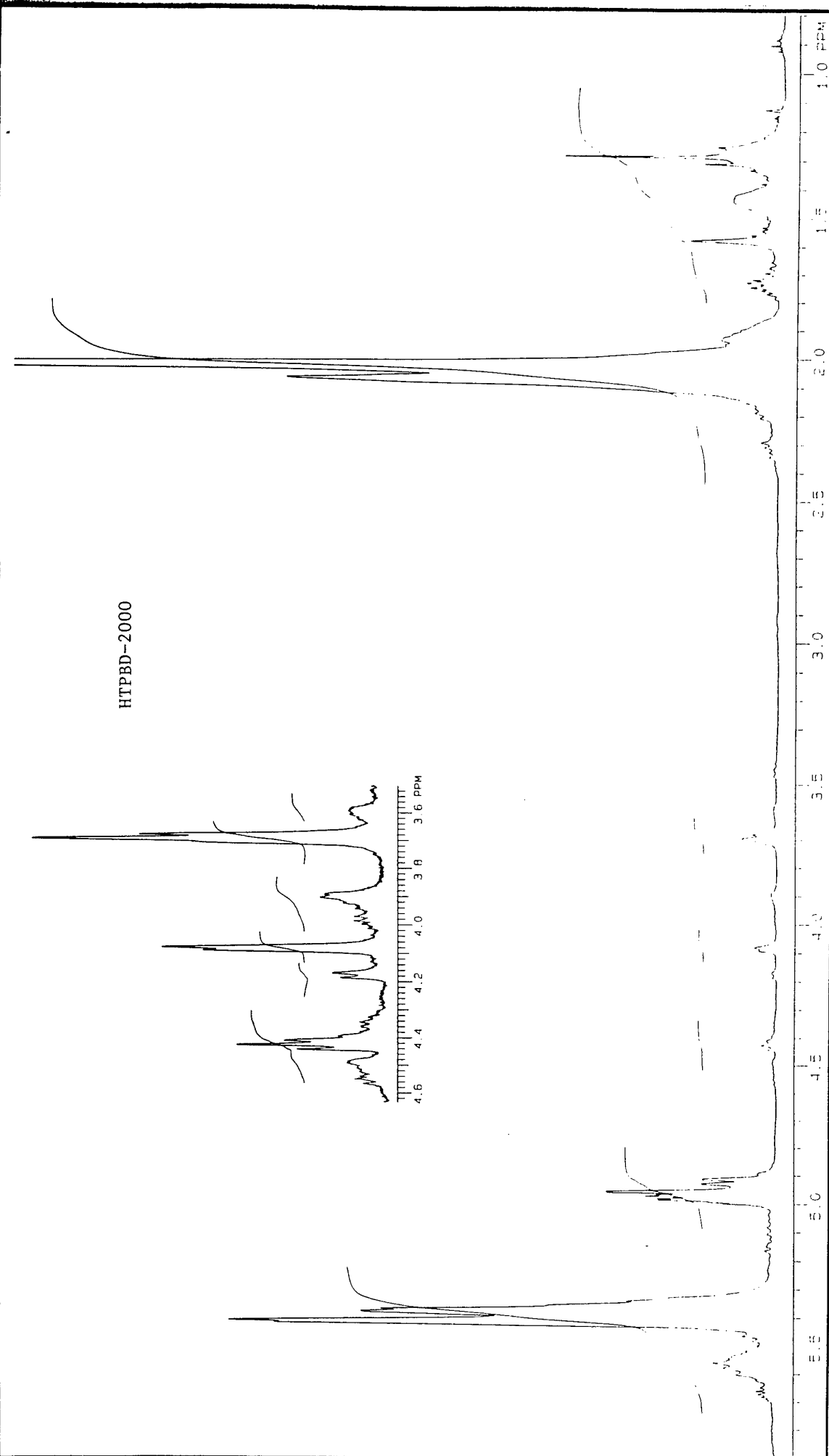
SAMPLE
 H-8219 (19414)
 137 (CDCL3)
 KESZLER B./E.O.

Number ---
 File H
 Date 05-01-96
 XL VXR 400variation

EXPERIMENT
 CDCL3

OBSERVE
 PLOT/PROCESSING

HTPBD-2000



Number HBE162
 File 13-09-9E
 Date YXR 400 VBT

SAMPLE
 H-7378 (18600)
 POLIBUTADIEN (CCCL3) 78u-121
 KESZLER B./E. O.

Pulse Sequence STC14
 Tube CD mm
 Temp °C
 Solvent CCCL3

EXPERIMENT
 FN SE SE sec CD sec
 LB Hz AF sec CCD sec
 Width 2040 Hz Sum 319.8 Hz/gpm
 Reference

PLOT/PROCESSING
 Nucleus 13C H₁ 75.0 Hz
 Mode 20 Power db
 Modulation C Freq 200 Hz
 Pulse Width µsec Power Mode

DECOUPLE
 Nucleus 13C M₁ 400 MHz
 Sec Width 5000.0 Hz Other 327.0 Hz
 Acc Time 3.374 sec Delay 0 sec
 Pulse Width 7.0 µsec Transients 16

OBSERVE

Number _____ H
 File 21-06-91
 Date _____
 VXR 400
 XL _____

SAMPLE
 H-7096 (118362)
 11B (CDCL3)
 KESZLER B./III.11.
 PROTON SURVEY/G.E.

Pulse Sequence: STD14
 Tube OD: _____ mm
 Temp: _____ °C
 Solvent: CDCL3

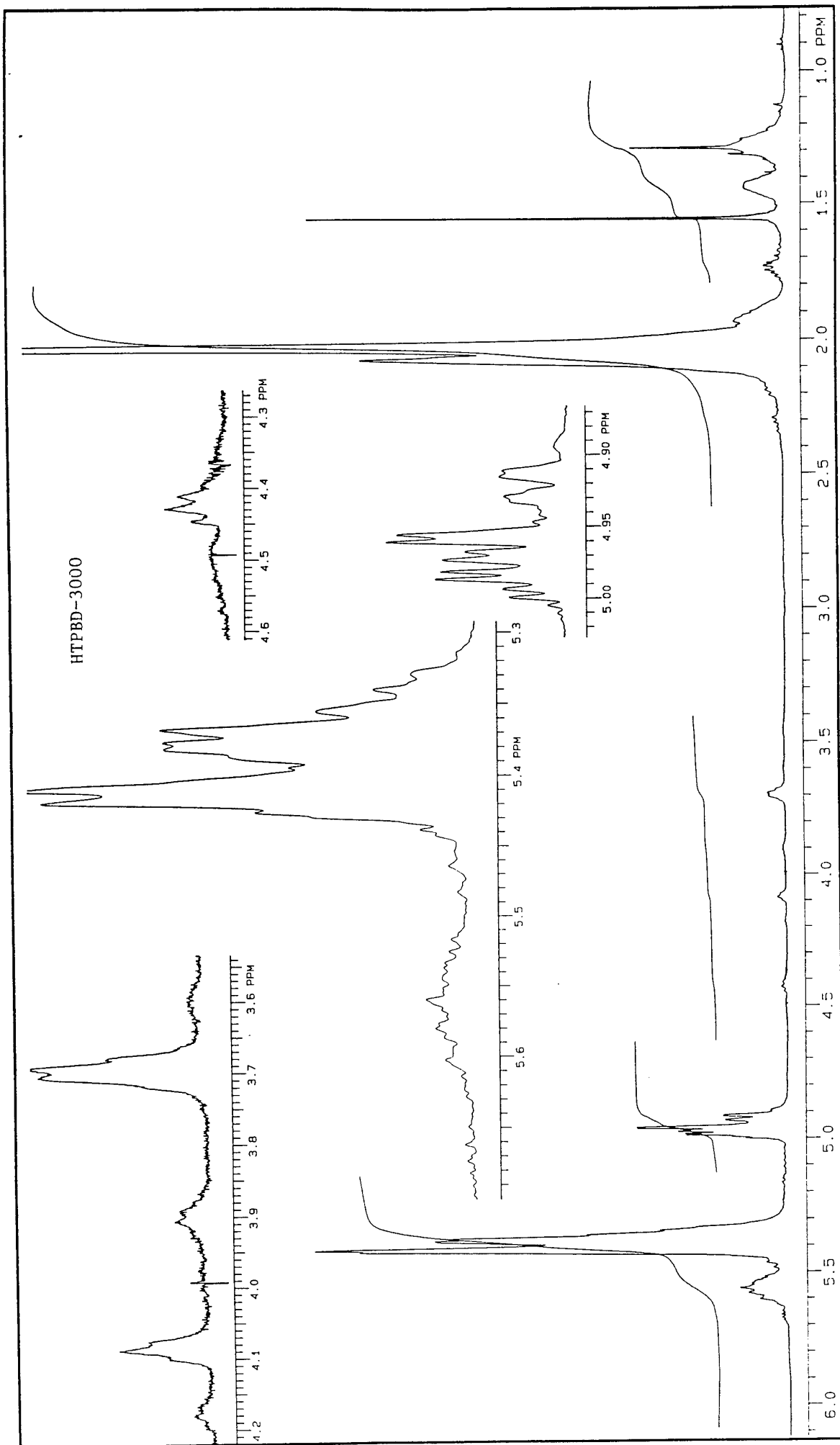
EXPERIMENT
 FN: 32 k RE _____ sec CD _____ sec
 LB: _____ Hz AF _____ sec CCD _____
 Width: 2139.0 Hz ppm Sum 308.1 Hz/ppm
 Reference: _____

PLOT/PROCESSING
 Nucleus: 1.750
 Mod: NNN
 Modulation Mod: C
 Pulse Width: _____ µsec
 Offset: _____ Hz
 Power: 20 db
 Freq: 200 Hz
 Power Mod: _____

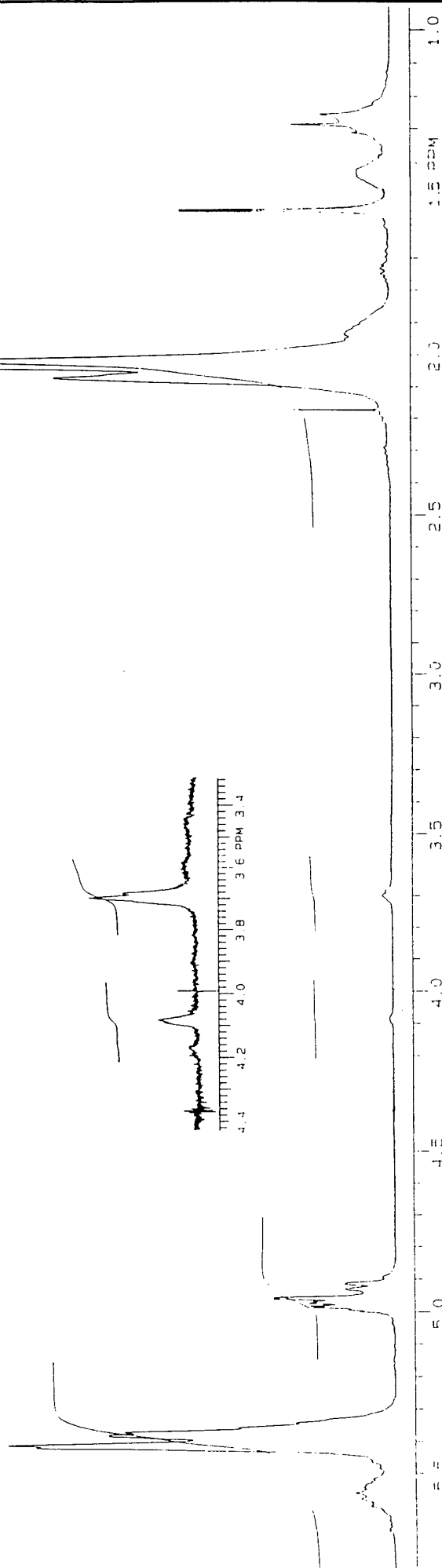
DECOUPLE
 Nucleus: 400 MHz
 Freq: -174.8 Hz
 Spec Width: 4000.0 Hz
 Offset: 0 Hz
 Acq Time: 4.000 sec
 Delay: 0 sec
 Transients: 32
 Pulse Width: 7.0 µsec

OBSERVE
 Nucleus: 1.750
 Freq: 400 MHz
 Spec Width: 4000.0 Hz
 Offset: -174.8 Hz
 Acq Time: 4.000 sec
 Delay: 0 sec
 Transients: 32
 Pulse Width: 7.0 µsec

HTPBD-3000



HTPBD -5000



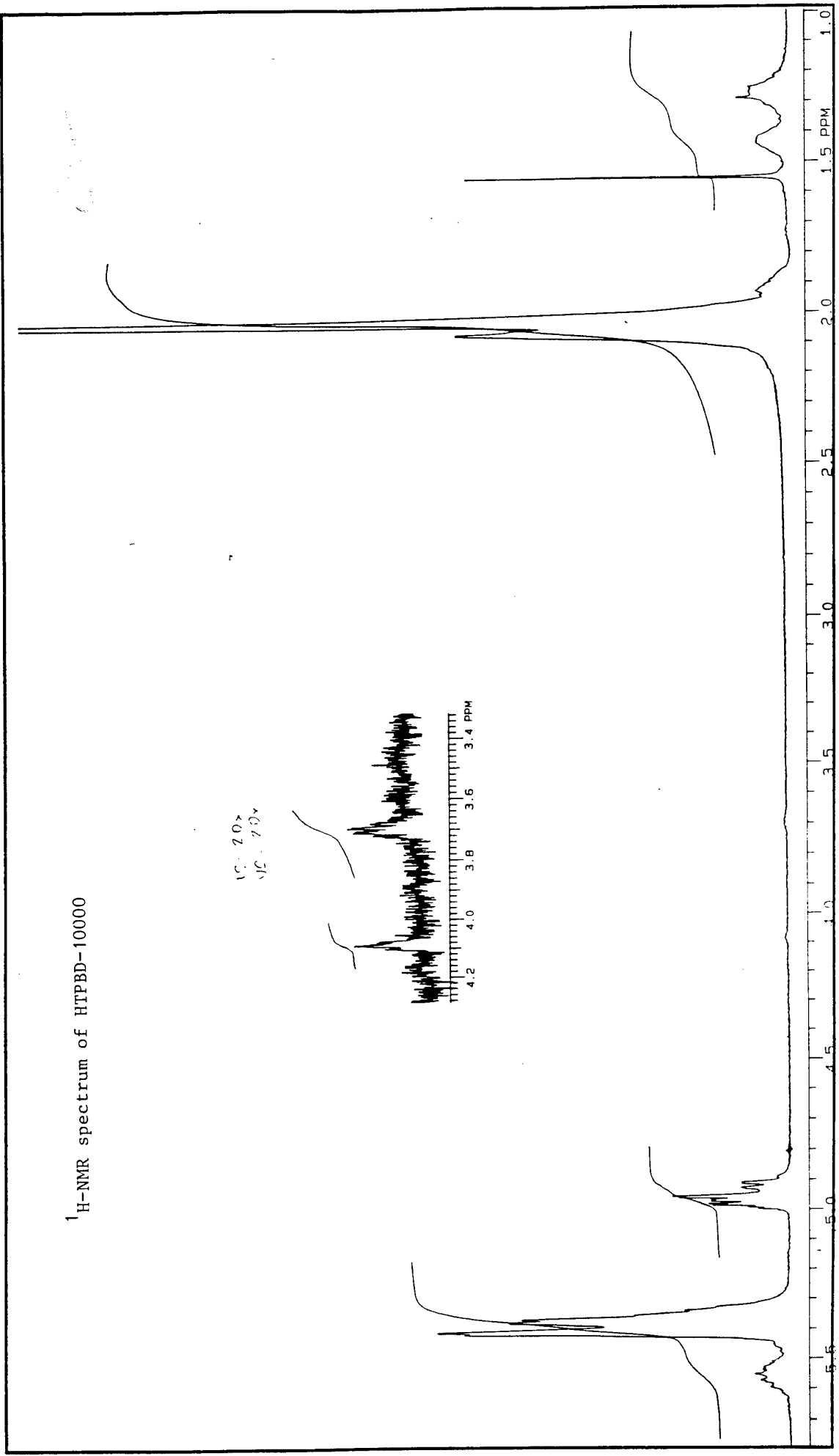
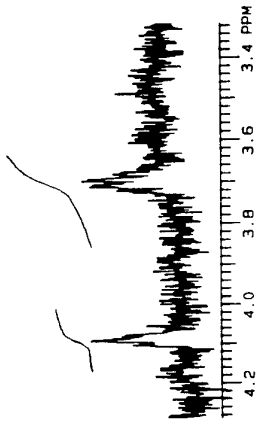
OBSERVE		Name: _____		Date: _____	
Spec Width	5000.0 Hz	Mode	NHN	Power	20 db
Acq Time	4.000 sec	Modulation Mode	C	Freq	200 Hz
Pulse Width	7.0 μ sec	Pulse Width	_____ μ sec	Power Mode	_____
DECOUPLE		Name: _____		Date: _____	
Spec Width	400 MHz	Mode	NHN	Power	20 db
Acq Time	1.750 sec	Modulation Mode	C	Freq	200 Hz
Pulse Width	7.0 μ sec	Pulse Width	_____ μ sec	Power Mode	_____
PLOT/PROCESSING		Name: _____		Date: _____	
Spec Width	372.3 Hz	Mode	NHN	Power	20 db
Acq Time	19.47.1 Hz	Modulation Mode	C	Freq	200 Hz
Pulse Width	7.0 μ sec	Pulse Width	_____ μ sec	Power Mode	_____
EXPERIMENT		Name: _____		Date: _____	
Spec Width	372.3 Hz	Mode	NHN	Power	20 db
Acq Time	19.47.1 Hz	Modulation Mode	C	Freq	200 Hz
Pulse Width	7.0 μ sec	Pulse Width	_____ μ sec	Power Mode	_____
SAMPLE		Name: _____		Date: _____	
Spec Width	372.3 Hz	Mode	NHN	Power	20 db
Acq Time	19.47.1 Hz	Modulation Mode	C	Freq	200 Hz
Pulse Width	7.0 μ sec	Pulse Width	_____ μ sec	Power Mode	_____
STUDY		Name: _____		Date: _____	
Spec Width	372.3 Hz	Mode	NHN	Power	20 db
Acq Time	19.47.1 Hz	Modulation Mode	C	Freq	200 Hz
Pulse Width	7.0 μ sec	Pulse Width	_____ μ sec	Power Mode	_____



Number: K226H
File: 14-08-95
Date: YXR 400 Varian

¹H-NMR spectrum of HTPBD-10000

10:20
12:20



3A8380

Nucleus 1H Freq 400 MHz
 Spec Width 5000 Hz Offset 0 Hz
 Acq Time 3.994 sec Delay 0 sec
 Pulse Width 7.0 sec Transients 16

Nucleus 1H Mode HNMR Offset 15.0 Hz
 Modulation Mode C Power 20 dB
 Pulse Width 7.250 msec Modulation Rate 200 Hz
 Power Mode ---

Plot/Processing
 IN 32 K HE --- sec CD --- sec
 LB --- Hz AF --- sec CD --- sec
 Width 1917 Hz/ptm Start 386 Hz/ptm
 Reference ---

Experiment
 Pulse Sequence SIDAH
 Tube ID --- mm
 Temp --- °C
 Solvent CDCl3

Sample
 H-8221 (19414)
 HTPBD-10 (CDCl3)
 KESZLER B./E.O.

Number ---
 File H
 Date 05-01-96
 XL VXR 400varian

ANNEX 2

CHARACTERIZATION OF HTPPE SAMPLES

- ◆ Molecular weight distribution of precursor HTPBD-1000
- ◆ Molecular weight distribution of precursor HTPBD-1500
- ◆ Molecular weight distribution of precursor HTPBD-2000
- ◆ Molecular weight distribution of precursor HTPBD-3000
- ◆ Molecular weight distribution of precursor HTPBD-5000
- ◆ Molecular weight distribution of precursor HTPBD-10000
- ◆ FT-IR spectrum of precursor HTPBD-1000
- ◆ FT-IR spectrum of precursor HTPBD-1500
- ◆ FT-IR spectrum of precursor HTPBD-2000
- ◆ FT-IR spectrum of precursor HTPBD-3000
- ◆ FT-IR spectrum of precursor HTPBD-5000
- ◆ FT-IR spectrum of precursor HTPBD-10000
- ◆ Proton-NMR spectra of precursor HTPBD-1000 and hydrogenated product
- ◆ Proton-NMR spectra of precursor HTPBD-1500 and hydrogenated product
- ◆ Proton-NMR spectra of precursor HTPBD-2000 and hydrogenated product
- ◆ Proton-NMR spectra of precursor HTPBD-3000 and hydrogenated product
- ◆ Proton-NMR spectra of precursor HTPBD-5000 and hydrogenated product
- ◆ Proton-NMR spectra of precursor HTPBD-10000 and hydrogenated product

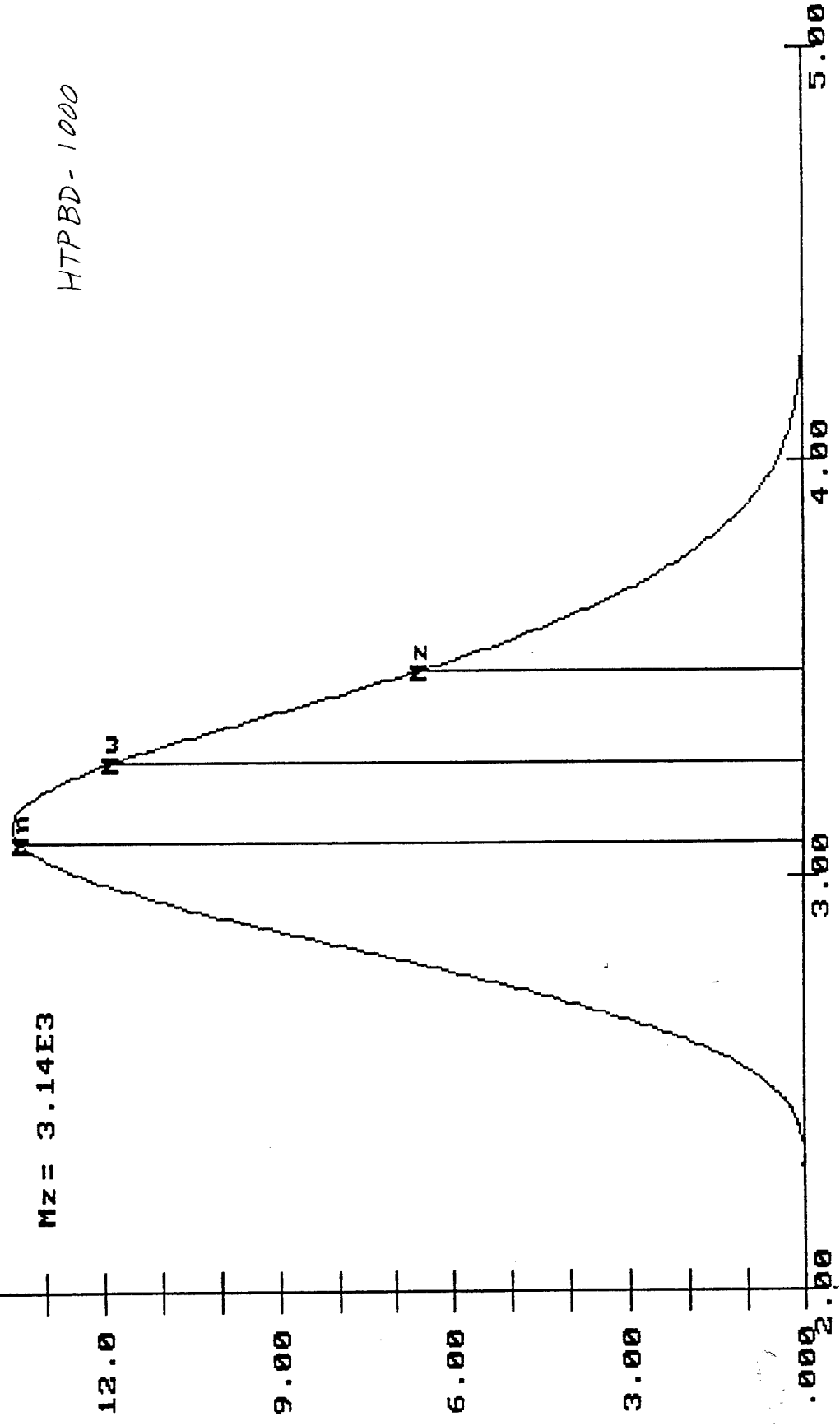
VISCOTEK CORP. UCAL 4.05 ENDED: 10/01/96 12:12
FILENAME: 1741a RUN ID: 96/182 Polibut. 174/1a

Mn = 1.21E3
Mw = 1.87E3
Mz = 3.14E3

MOLECULAR WEIGHT DISTRIBUTION

HTPBD-1000

T-101 X (M501) M

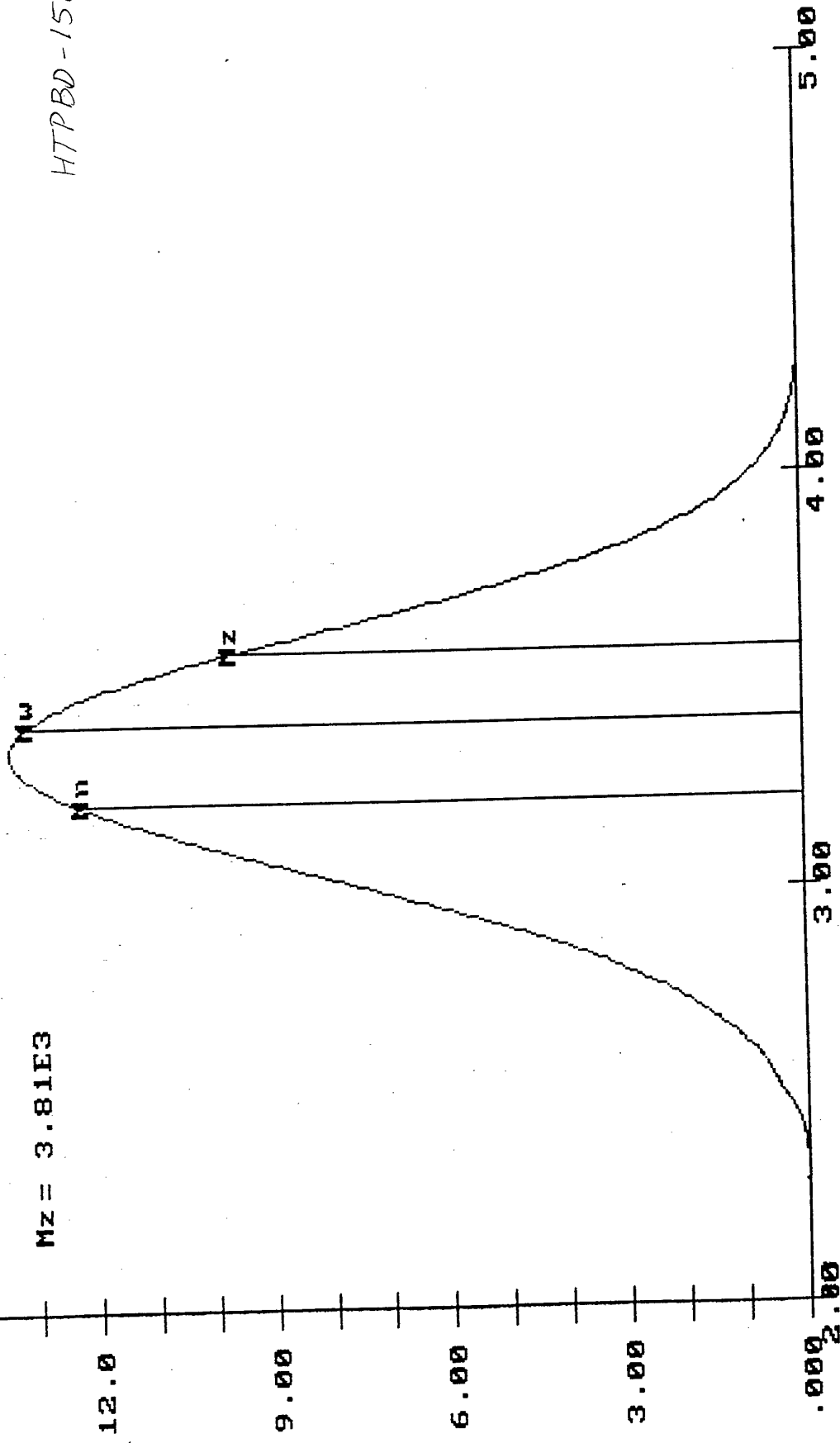


COTEK CORP. UCAL 4.05 ENDED: 10/01/96 13:26
ENAME: 174k2 RUN ID: 96/184 Polibut. 174/k2

Mn = 1.67E3
Mw = 2.55E3
Mz = 3.81E3

MOLECULAR WEIGHT DISTRIBUTION

HTPB00-1500

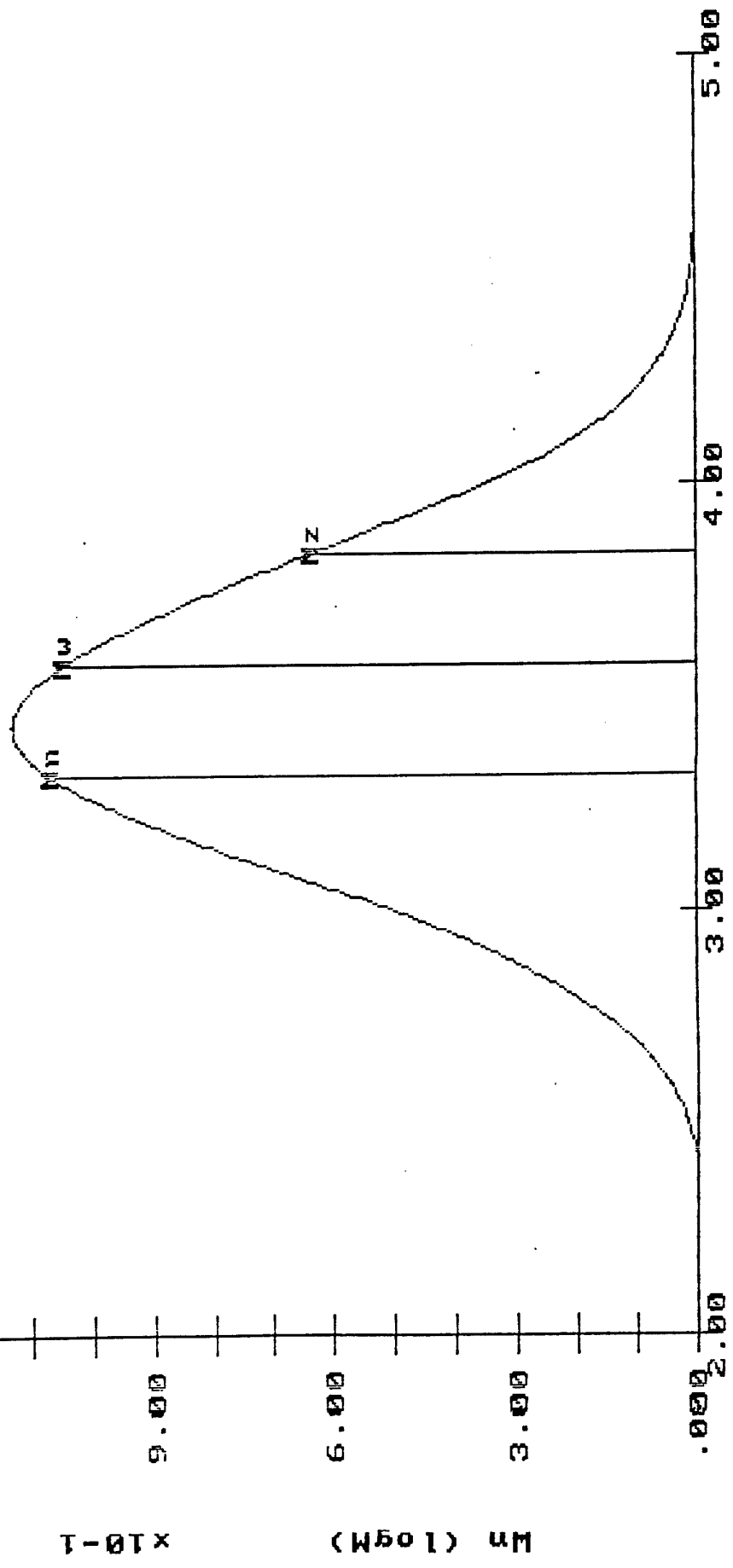


USCOTEM CORP. UCAL 4.05 ENDED: 09/24/96 12:01
FILENAME: 161K RUN ID: 96/175 Polibut. 161/K

MOLECULAR WEIGHT DISTRIBUTION

HTPBD 2000

Mn = 2.14E3
Mw = 3.83E3
Mz = 6.92E3



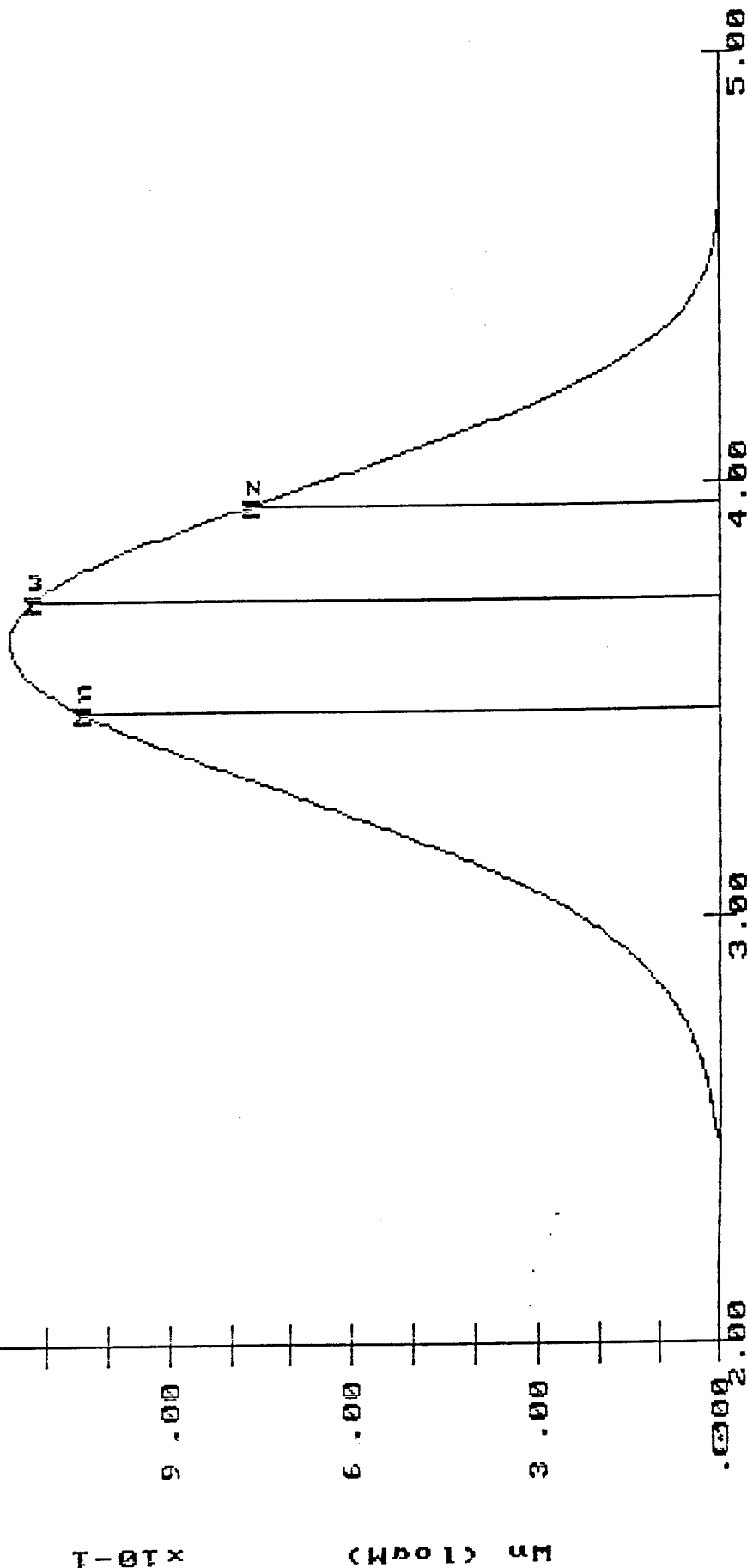
LOG M

VISCOSEK CORP. UCAL 4.05 ENDED: 08/13/96 13:45
FILENAME: 154160 RUN ID: 96/143 Polibut. 154,160 mnta

Mn = 3.06E3
Mw = 5.44E3
Mz = 9.06E3

MOLECULAR WEIGHT DISTRIBUTION

HTPBD 3000



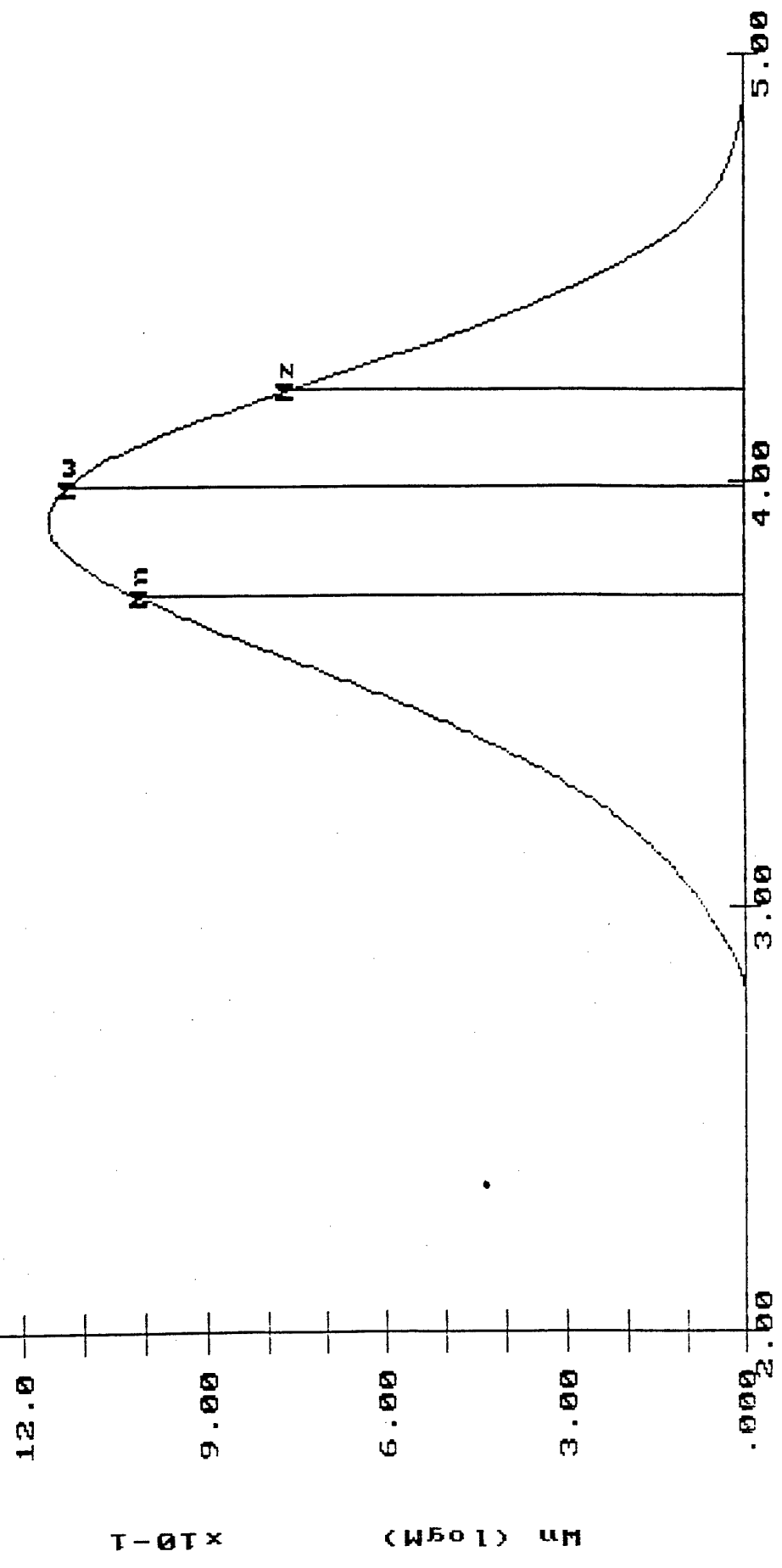
INC M

FILENAME: 1751 RUN ID: 96/185 Polibut. 175/1

Mn = 5.40E3
Mw = 9.76E3
Mz = 1.63E4

MOLECULAR WEIGHT DISTRIBUTION

HTP BD-5000



LOG M

Wt (%)

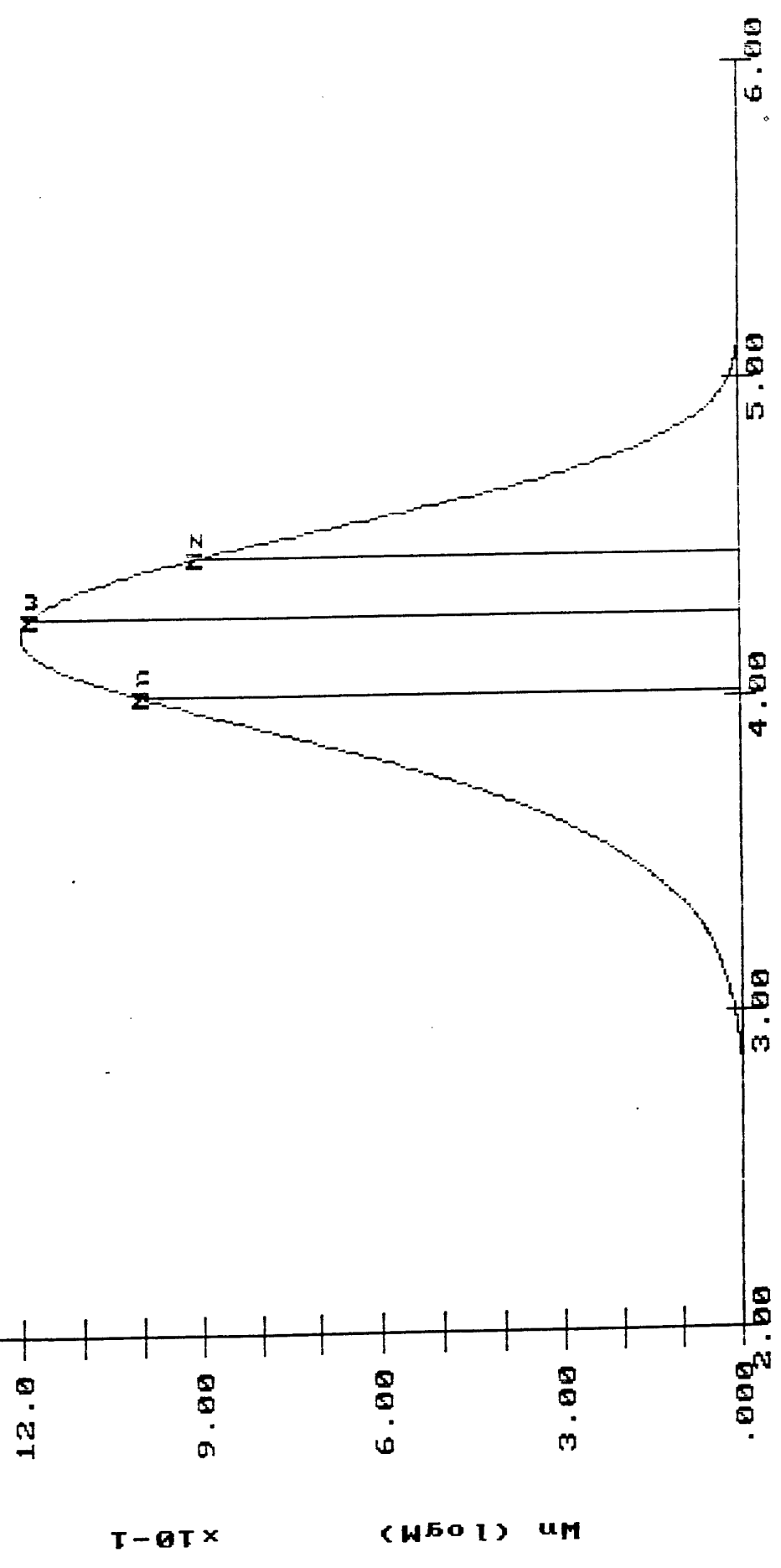
(M501) Wt

VISCO TEK CORP. UCAL 4.05 ENDED: 09/09/96 12:55
FILENAME: 167fob RUN ID: 96/158 Polibut. 167/fob

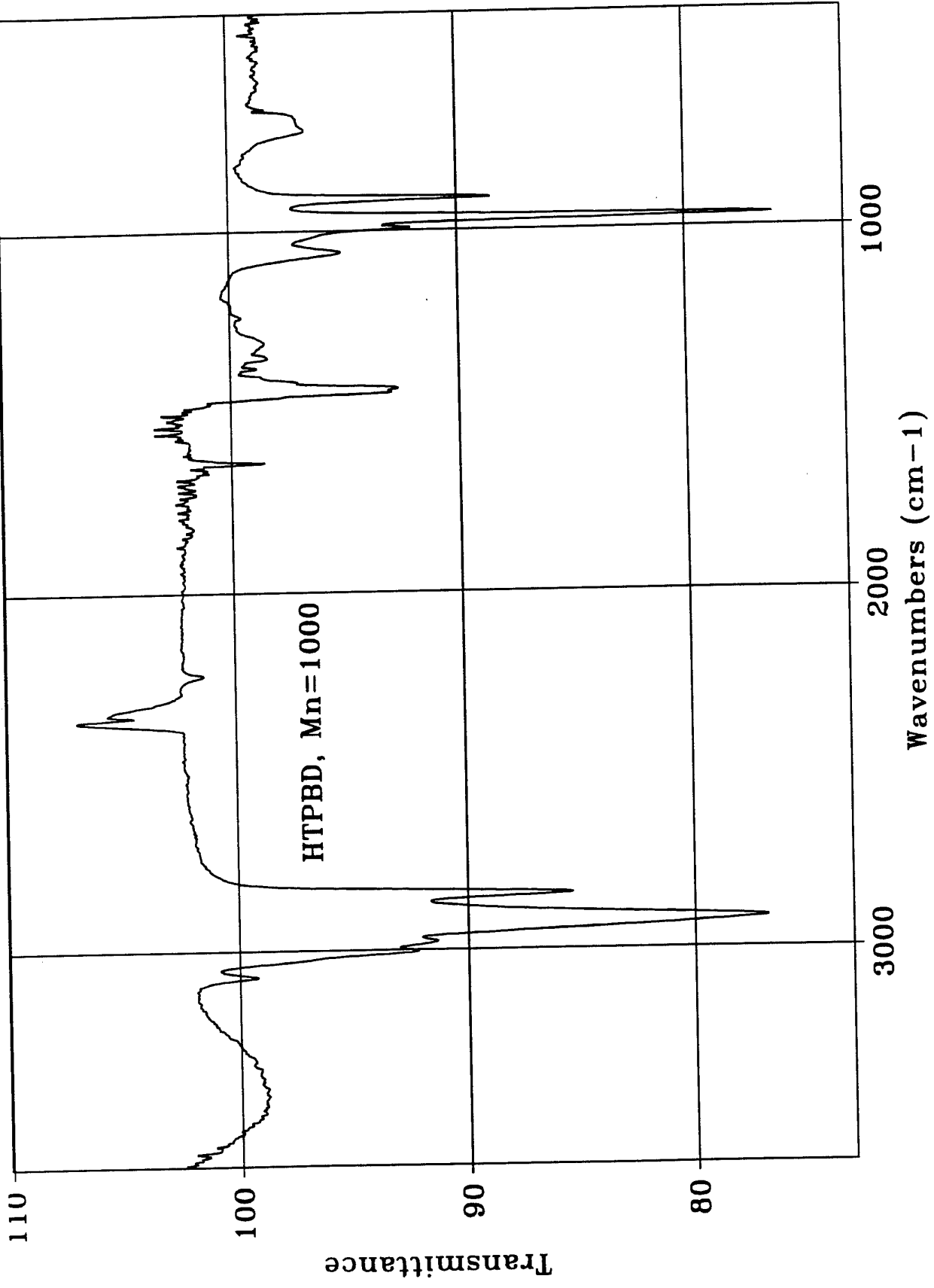
Mn = 1.03E4
Mw = 1.83E4
Mz = 2.86E4

MOLECULAR WEIGHT DISTRIBUTION

HTPBD - 10000

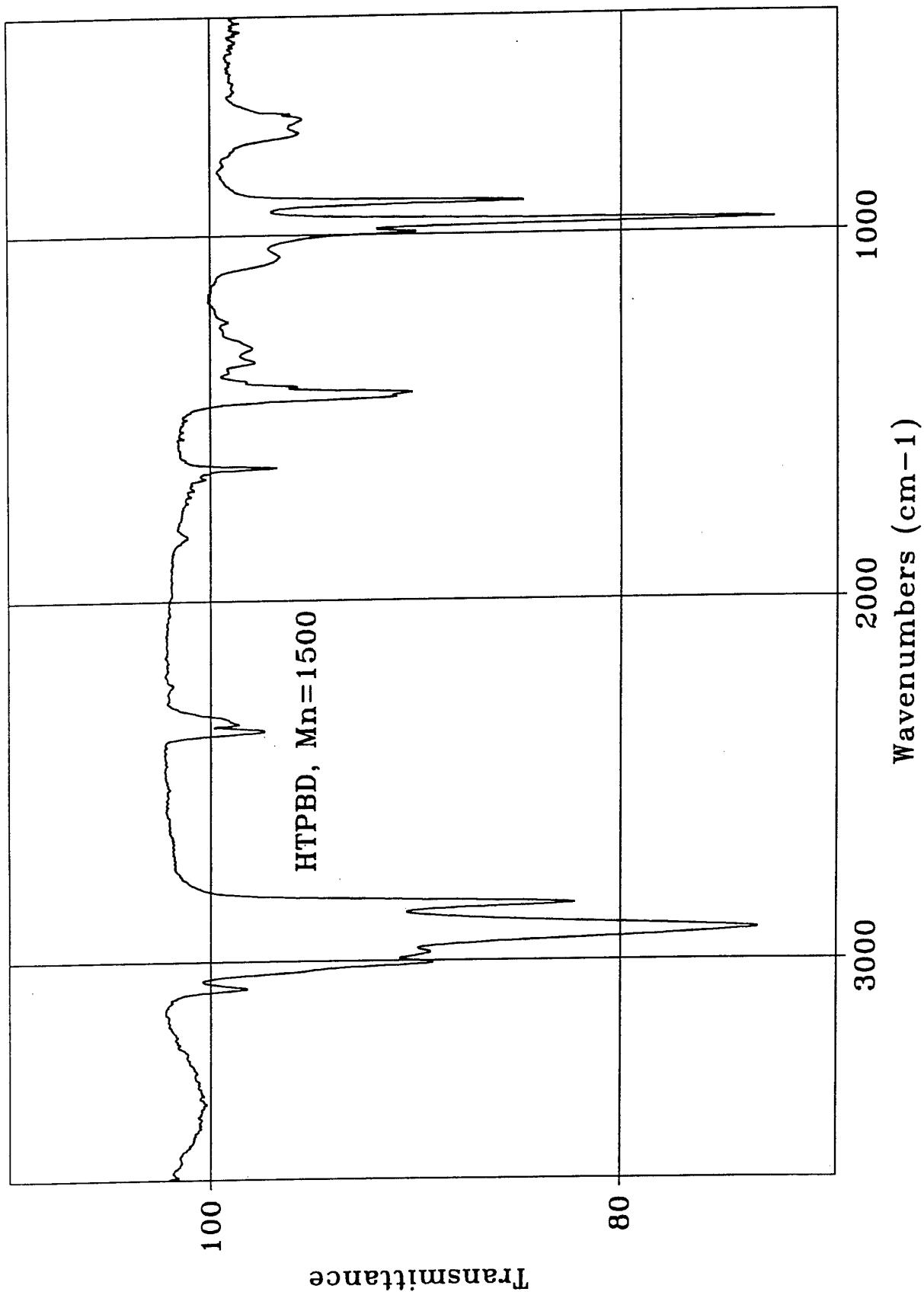


LOG M



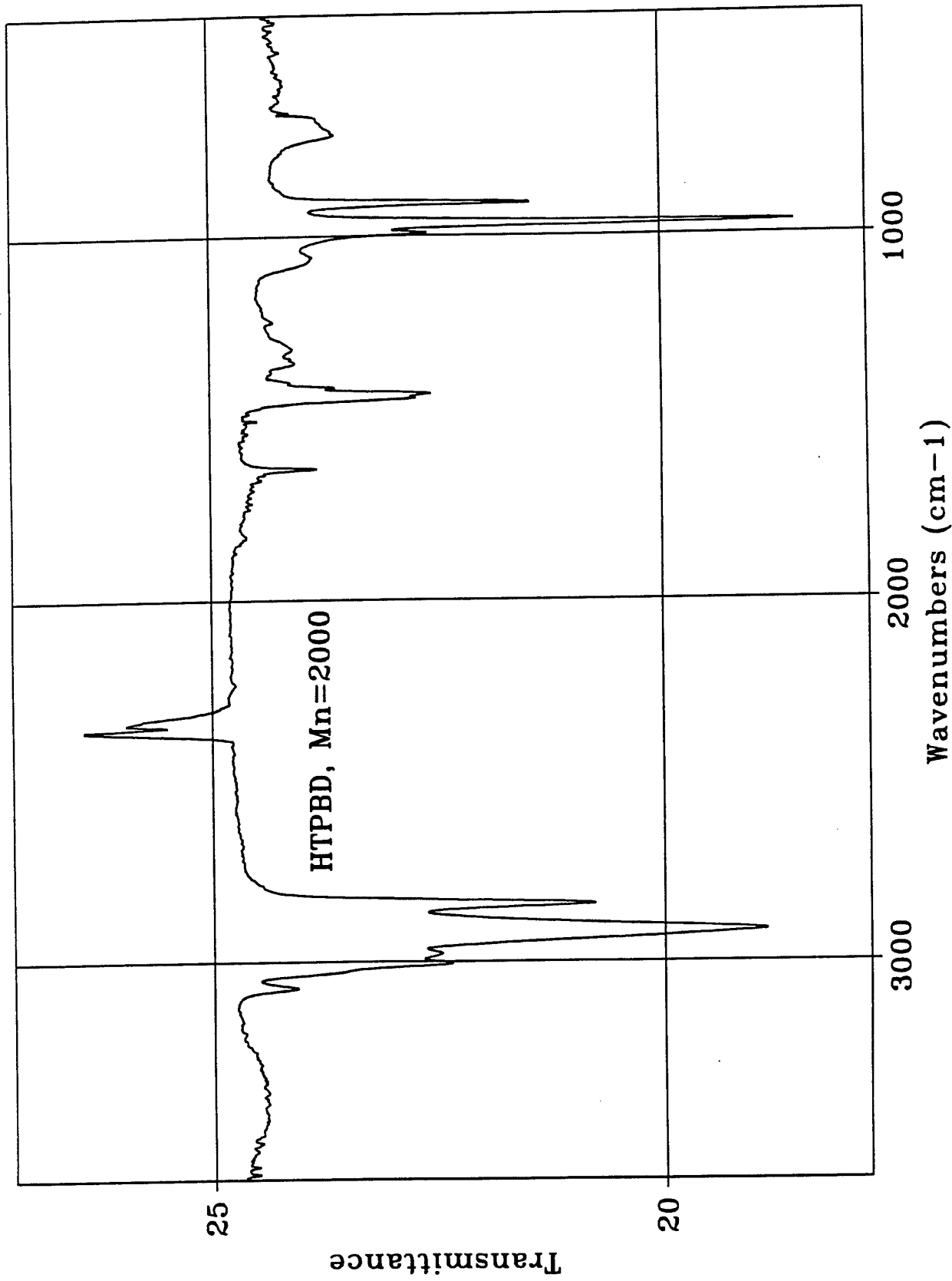
01/29/97 02:28

Res= 4 cm-1



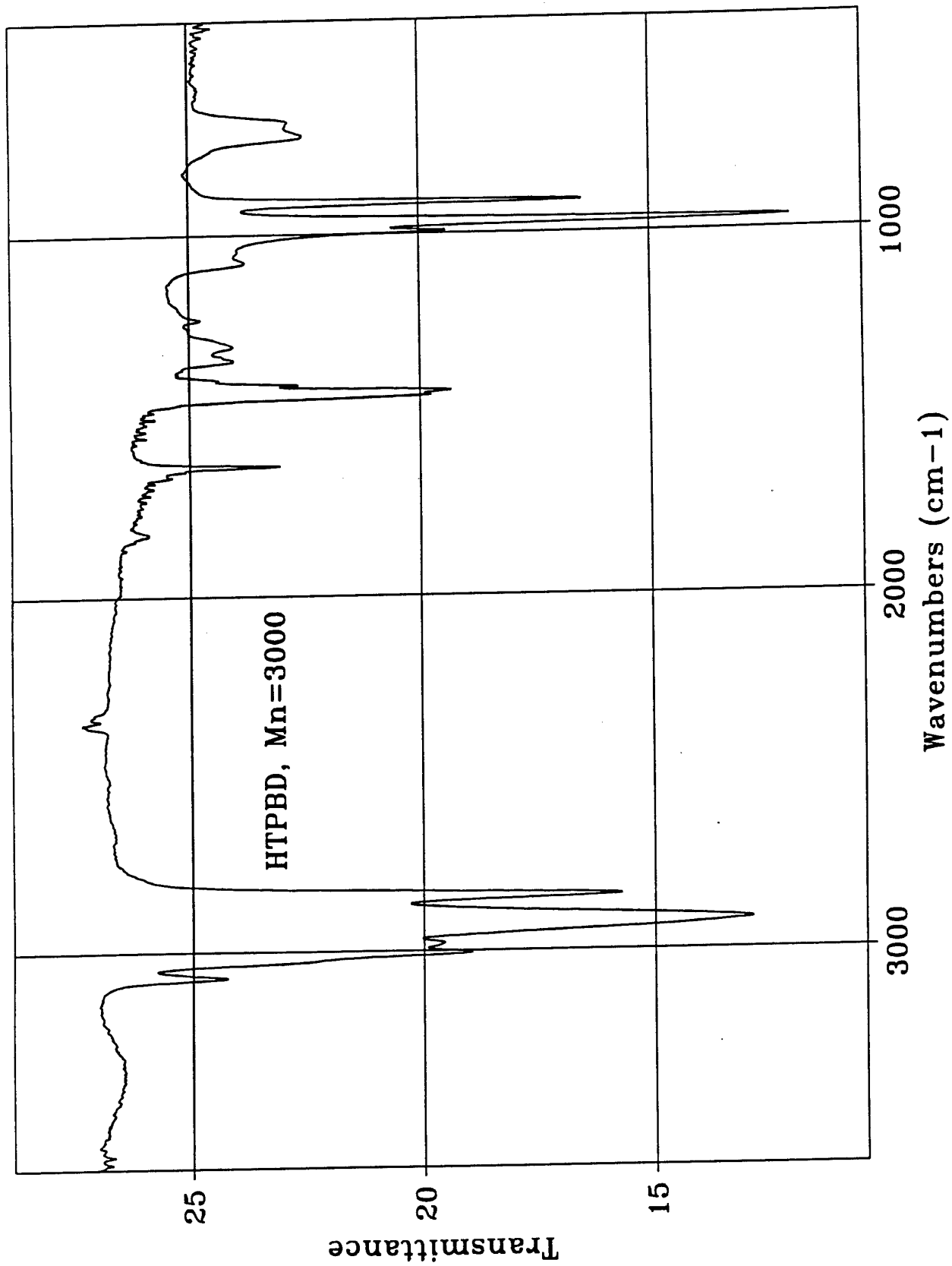
Res= 4 cm-1

01/29/97 02:37



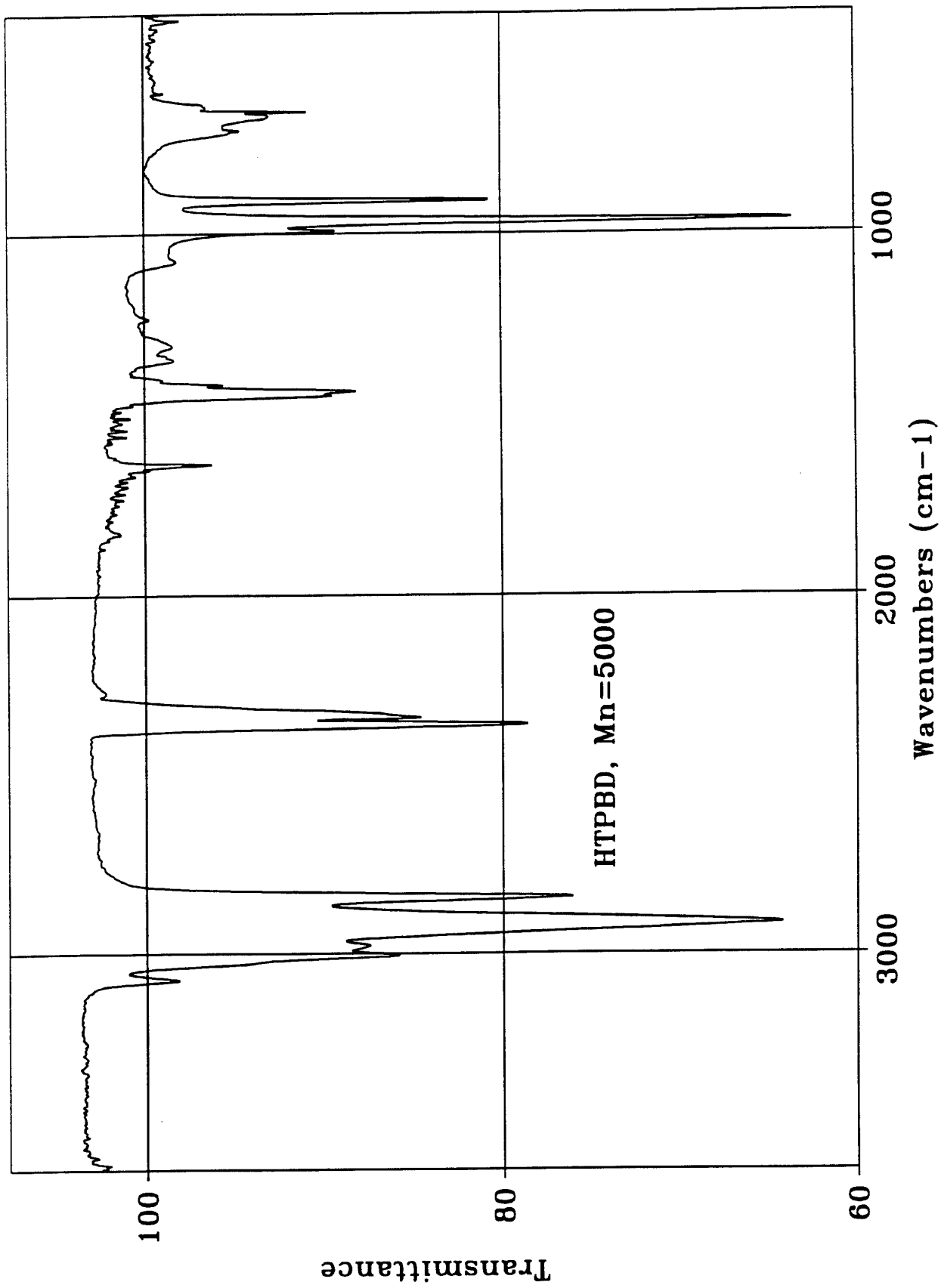
01/29/97 02:45

Res= 4 cm-1



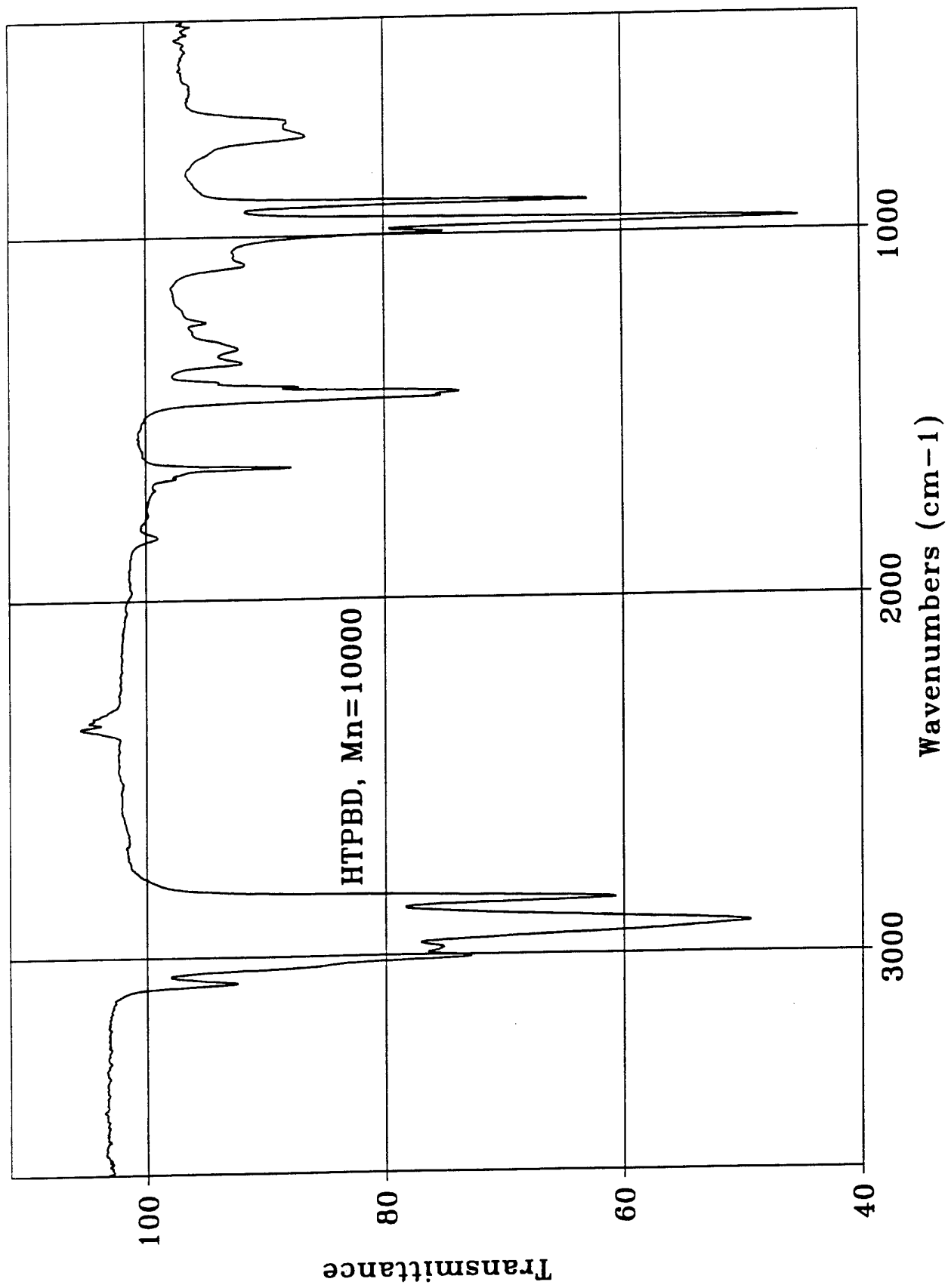
01/29/97 02:52

Res= 4 cm-1



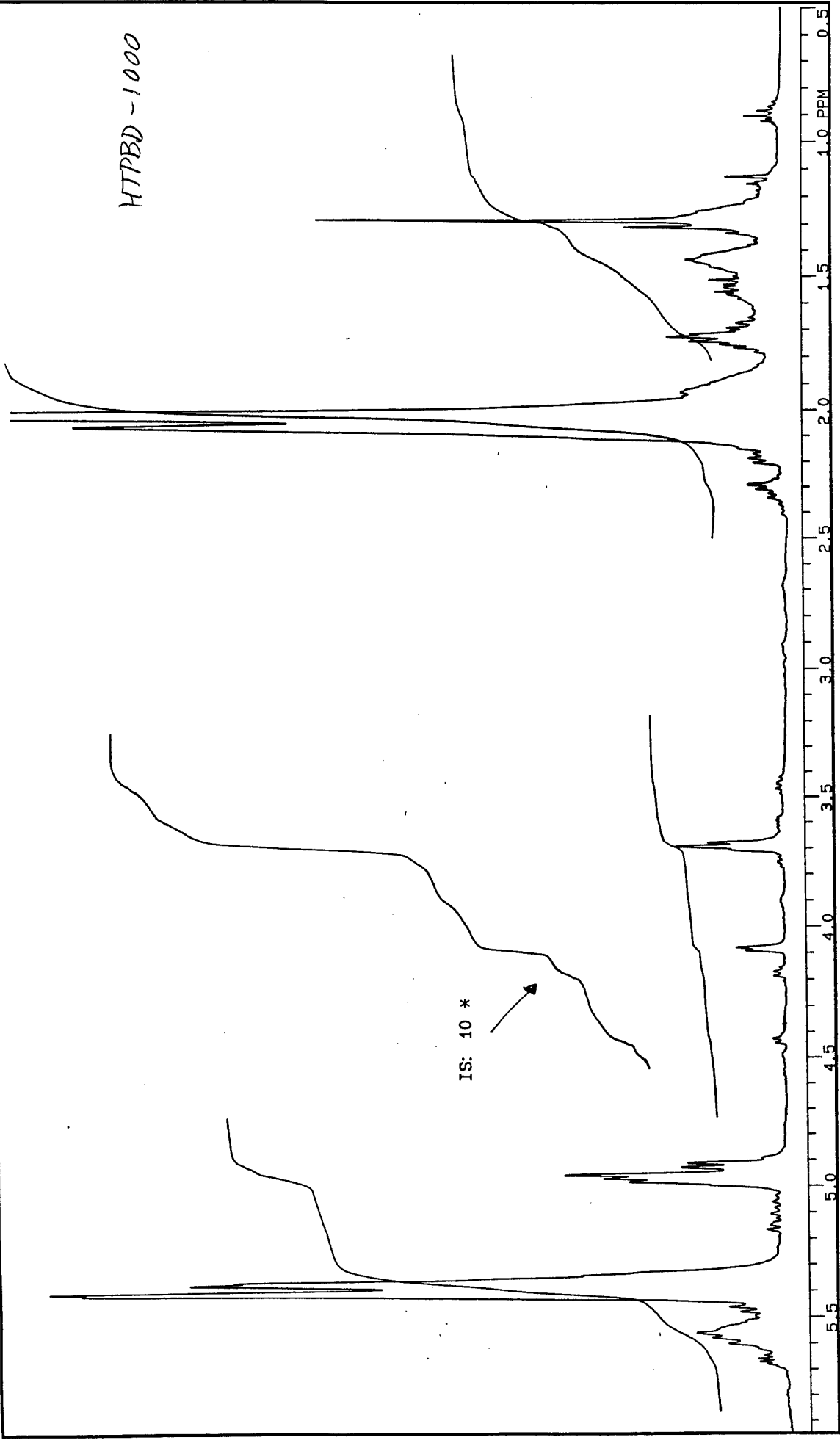
HTPBD, Mn=5000

Res= 4 cm⁻¹



Res= 4 cm-1

HTPBD-1000



Number _____
 File _____ H
 Date 08-10-96
 XL YXR 400variation

SAMPLE
 H-9920 (21023)
 HTPBD-1E3 (CDCL3)
 KELLER F./G.E.

Pulse Sequence SID1H
 Tube OD _____ mm
 Temp _____ °C
 Solvent CDCL3

EXPERIMENT

PH 32 K RE _____ sec CD _____ sec
 LB _____ Hz AF _____ sec CD _____ sec
 Width 2180.1 Hz/ppm Start 198.8 Hz/ppm
 Reference _____

PLOT/PROCESSING

Nucleus 1.750 MHz
 Mode NNN
 Modulation Mode C
 Pulse Width _____ μsec

Offset 75.0 Hz
 Power 20 db
 Freq 200 Hz
 Power Mode _____

RECOUPLE

Nucleus 1.750 MHz
 Spec Width 5988.8 Hz
 Acq Time 3.995 sec
 Pulse Width 7.0 μsec

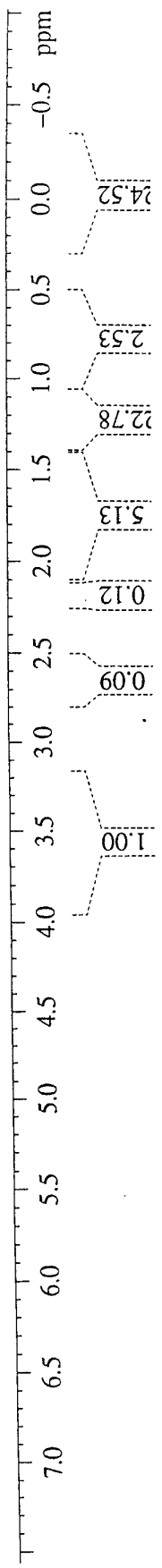
Freq 400 MHz
 Offset -174.8 Hz
 Delay 0 sec
 Transients 16

OSSENSE

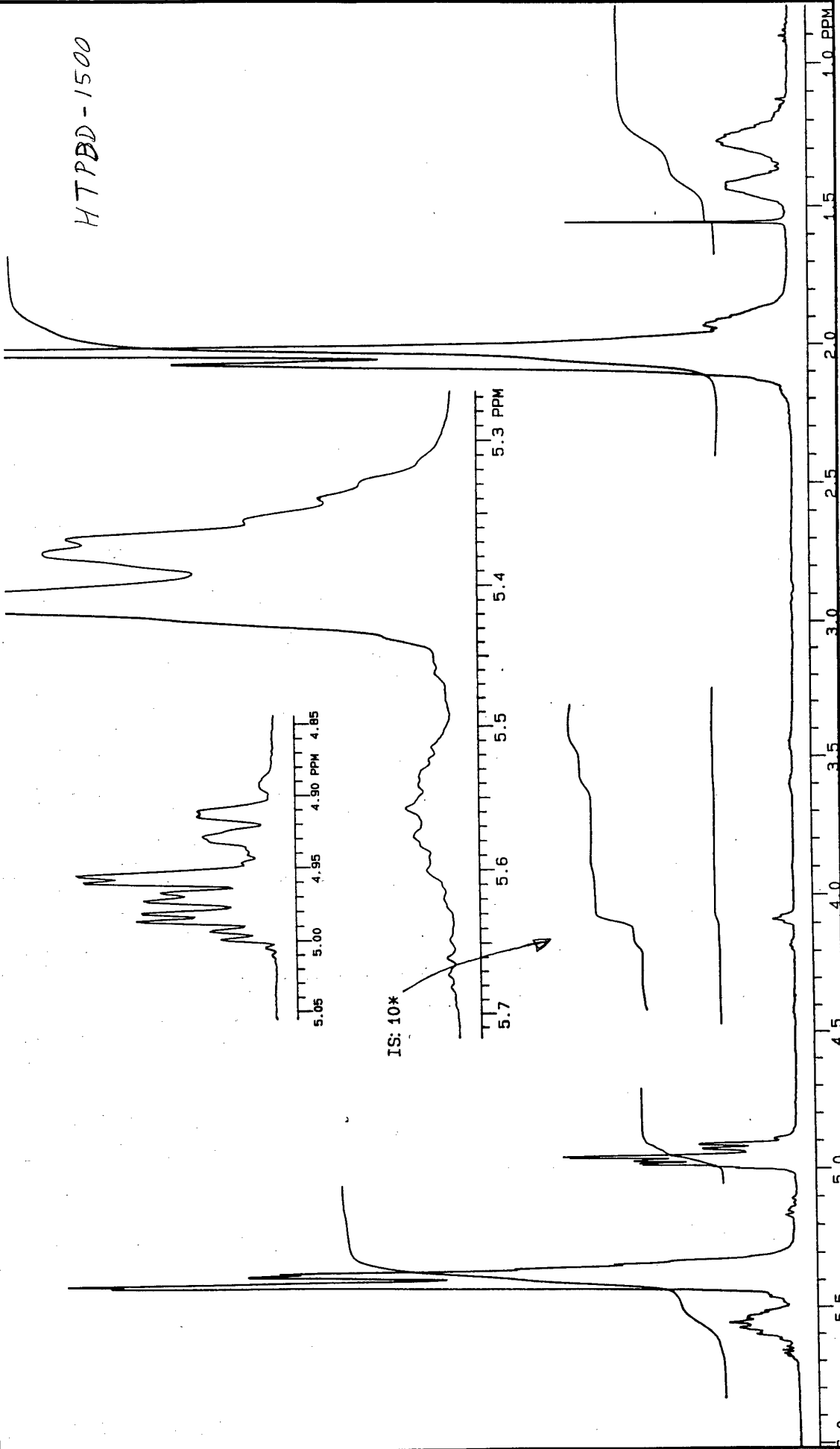
7.25
5.10
5.38
3.85
3.70
3.63
-2.64
-2.16
-1.97
-1.72
-1.69
-1.63
-1.56
-1.45
-1.30
-1.29
-1.25
-1.13
-0.97
-0.95
-0.94
-0.92
-0.90
-0.89
-0.88
-0.86
-0.83
-0.82
-0.80
-0.11
-0.01
-0.01
-0.13

HTPE-1000

HTPBD-1000Reduced D0596/1/1
1H Op.: angela 1997 May 21
CDC13 Nooff T=300.0K NS=16



HTPBD-1500



Number _____
 File H
 Date 08-10-96
 XL YXR 400 VARIAN

SAMPLE
 H-9917 (21023)
 HTBD-SE3 (CDCL3)
 KELLER F./G.E.
 Pulse Sequence STD1H
 Tube O.D. _____ mm
 Temp. _____ °C
 Solvent CDCL3

EXPERIMENT
 PN 32 K RE _____ sec OD _____ sec
 LB _____ Hz AF _____ sec CD _____
 Width 2085 G Hz/ppm Start 321 Hz/ppm
 Reference _____

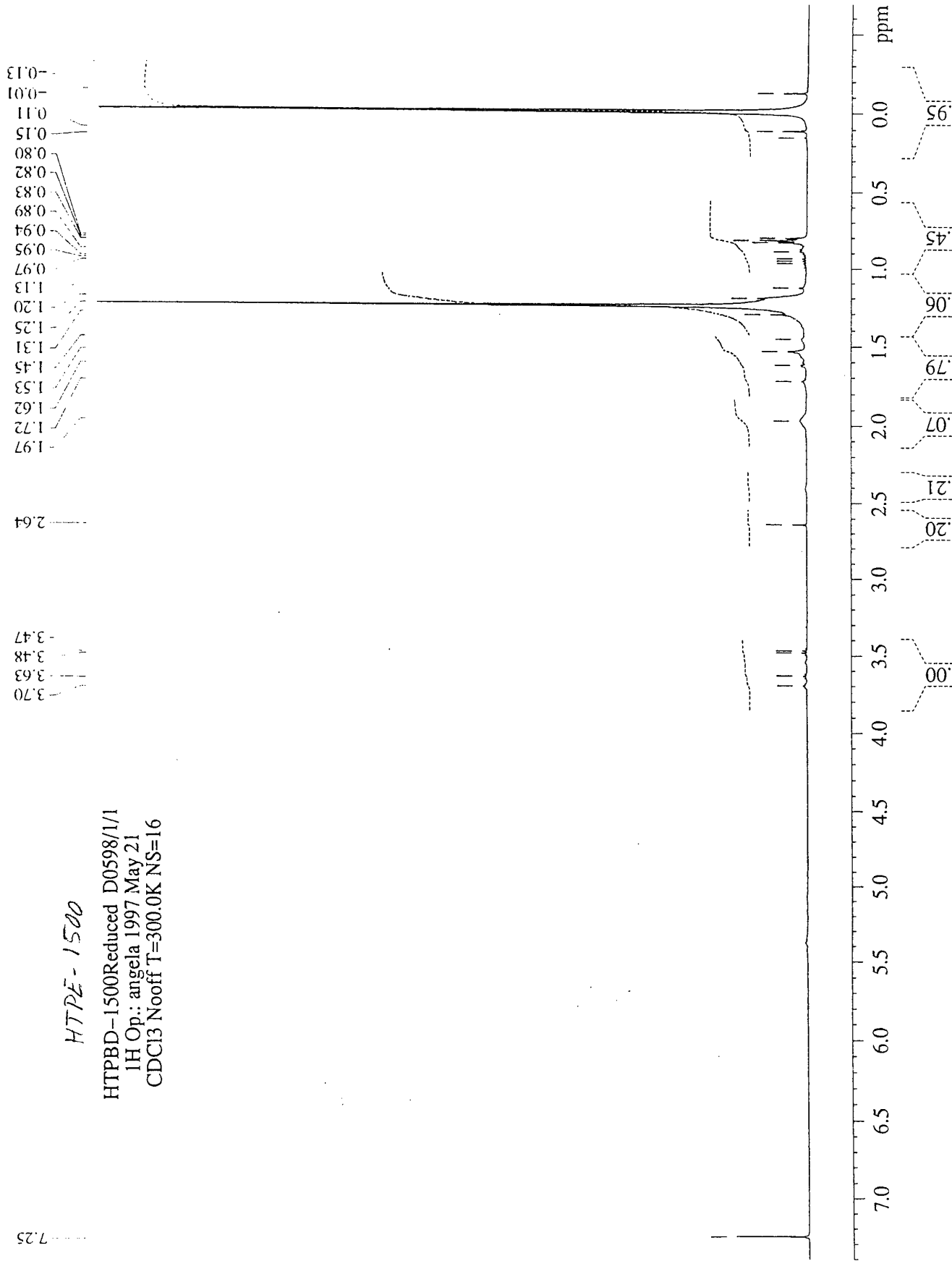
PLOT/PROCESSING
 Nucleus 1 750 MHz Other 75 Hz
 Mode NM Power 20 dB
 Modulation: Mode C Freq. 200 Hz
 Pulse Width _____ msec Power Mode _____

RECORPLE
 Nucleus 1 750 MHz Freq. 400 MHz
 Spec. Width 5908 Hz Offset -174 Hz
 Acq. Time 3.995 sec Delay _____ sec
 Pulse Width 7 msec Transients 16

OBSERVE

HTPE-1500

HTPBD-1500Reduced D0598/1/1
1H Op.: angela 1997 May 21
CDCl3 Nooff T=300.0K NS=16



HTPBD 2000

IS = 10 *



Number _____
File H
Date 08-10-95
XL VXR 400 variation

SAMPLE
H-9921 (21023)
HTPBD-2E3 (GDCL3)
KELLER F./G.E.

Pulse Sequence STD4H
Tube OD _____ mm
Temp _____ °C
Solvent GDCL3

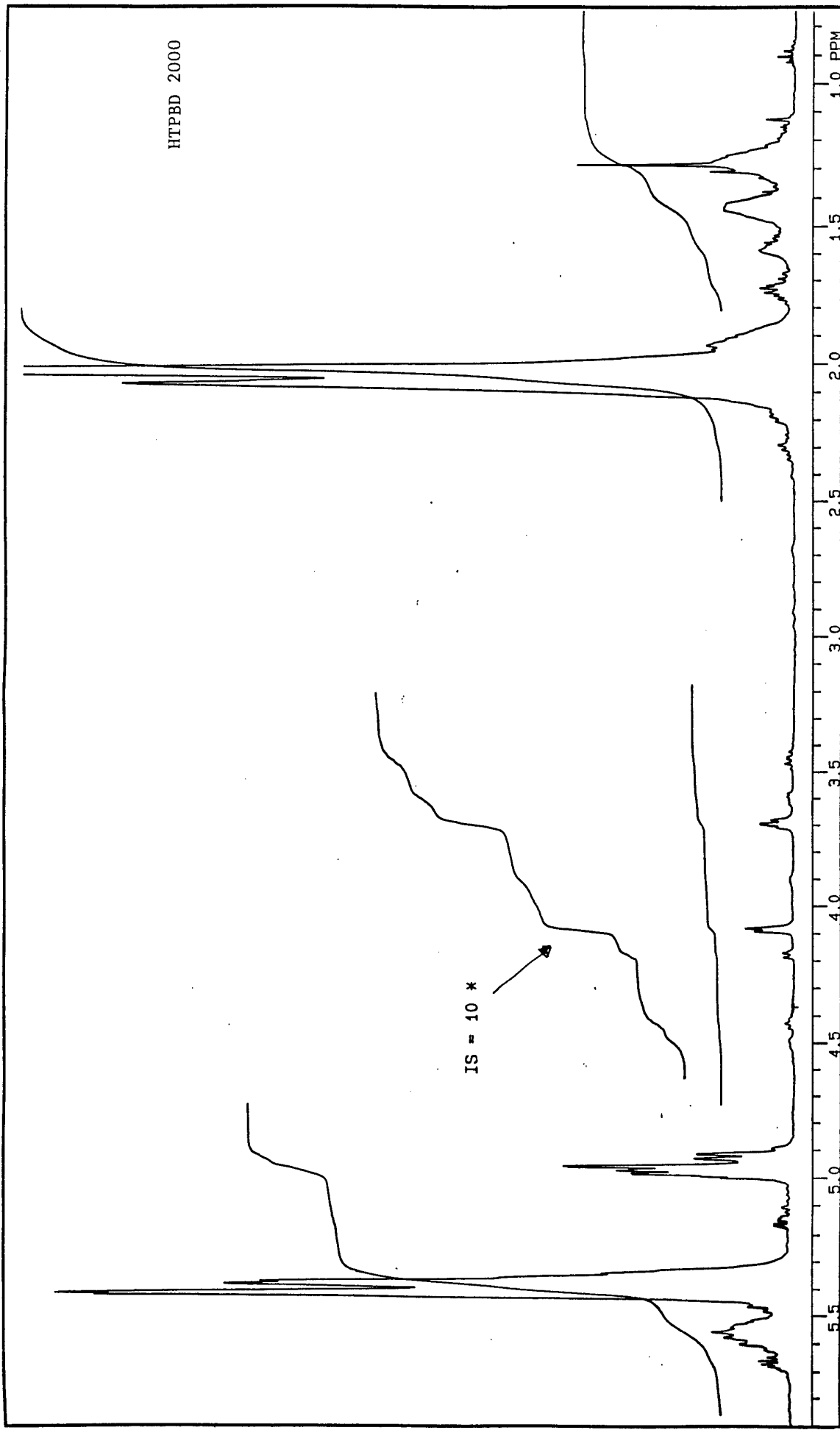
EXPERIMENT

PL01/PROCESSING
P1 32 K RE _____ sec CD _____ sec
L8 _____ Hz AF _____ sec CD _____ sec
Width 2062.2 Hz/gpm Start 298.4 Hz/gpm
Reference _____

Nucleus 1.750 Other 75.0 Hz
Mode NNN Power 20 db
Modulation Mode C Freq 200 Hz
Pulse Width _____ sec Power Mode _____

RECEIVE
Nucleus 1.750 Freq 400 MHz
Spec Width 5998.8 Hz Other 174.8 Hz
Acq Time 3.995 sec Delay 0 sec
Pulse Width 7.0 sec Transmits 15

OBSERVE
3A03000

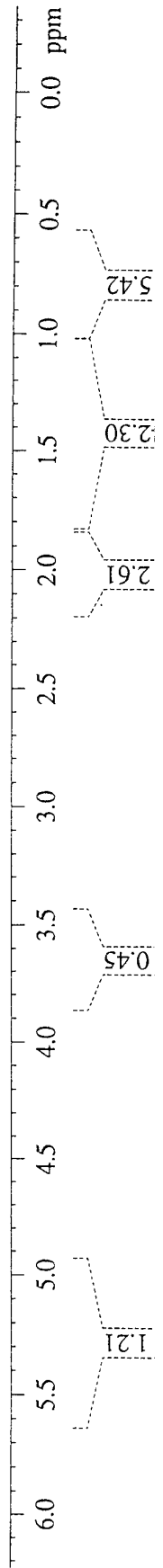


0.00
0.12
0.81
0.82
0.84
0.90
0.94
0.96
0.97
1.14
1.25
1.31
1.57
1.73
1.97

3.64
3.70

5.38

HTPE -2000
Reduced 2000
D0446/I/1 IH Op.: toni
CDCI3 Nooff T=300.0K NS=16



HTPBD 3000

$\text{CH}_2 - \text{C} \equiv \text{CH} - \text{CH}_2$

$\text{CH} - \text{CH} = \text{CH} - \text{CH}_2$
OH

$\text{CH}_2 - \text{C} \equiv \text{C} - \text{CH}_2$

$\text{CH} - \text{CH} = \text{CH} - \text{OH}$

$\text{CH}_2 - \text{CH}_2 - \text{OH}$

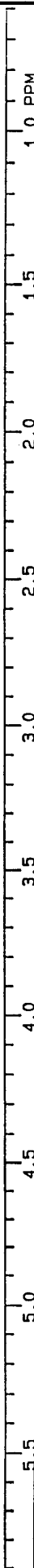
$\text{CH} - \text{CH} - \text{CH}_2 - \text{OH}$

IS = 10 *

$\text{CH} = \text{CH}_2$

$\text{CH}_2 - \text{CH}_2 - \text{CH} -$

$\text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2$



Nucleus: ^1H Freq: 400 MHz
 Spec. Width: 5998.8 Hz Offset: 174.8 Hz
 Acq. Time: 3.995 sec Delay: 0 sec
 Pulse Width: 7.0 μsec Transients: 16
 Nucleus: ^{13}C Freq: 100 MHz
 Spec. Width: 174.8 Hz Offset: 174.8 Hz
 Acq. Time: 3.995 sec Delay: 0 sec
 Pulse Width: 7.0 μsec Transients: 16

PLOT/PROCESSING
 FN: 32 X RE sec CD: sec
 LR: hr AF: sec CD: sec
 Width: 2126.7 Hz/ppm Start: 239.8 Hz/ppm
 Reference: CDCl_3

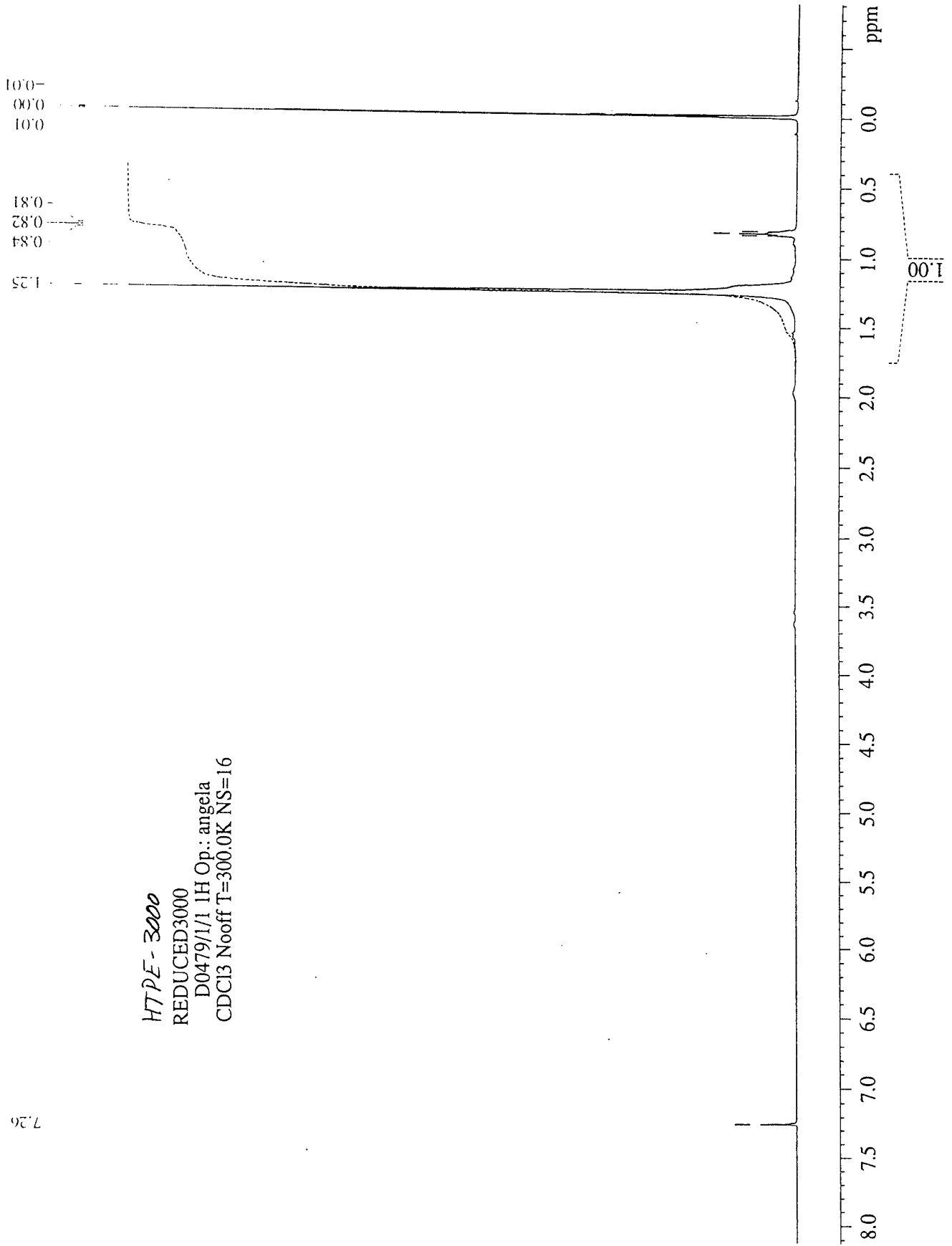
SAMPLE
 H-9922 (21023)
 HTPBD-3E3 (CDCl3)
 KELLER / S. E.

Number: _____
 File: KEEB3
 Date: 08-10-95
 XL: YXR 400 variation



7.26

HTPE-3000
REDUCED3000
D0479/1/1 1H Op.: angela
CDCI3 Nooff T=300.0K NS=16



HTPDB-5000

IS: 10 *



Number _____
File _____ H
Date: 08-10-98
XL VXR 400 varian

SAMPLE
H-9919 (21023)
HTPDB-1.5E3 (CDCL3)
KELLER F./G.E.

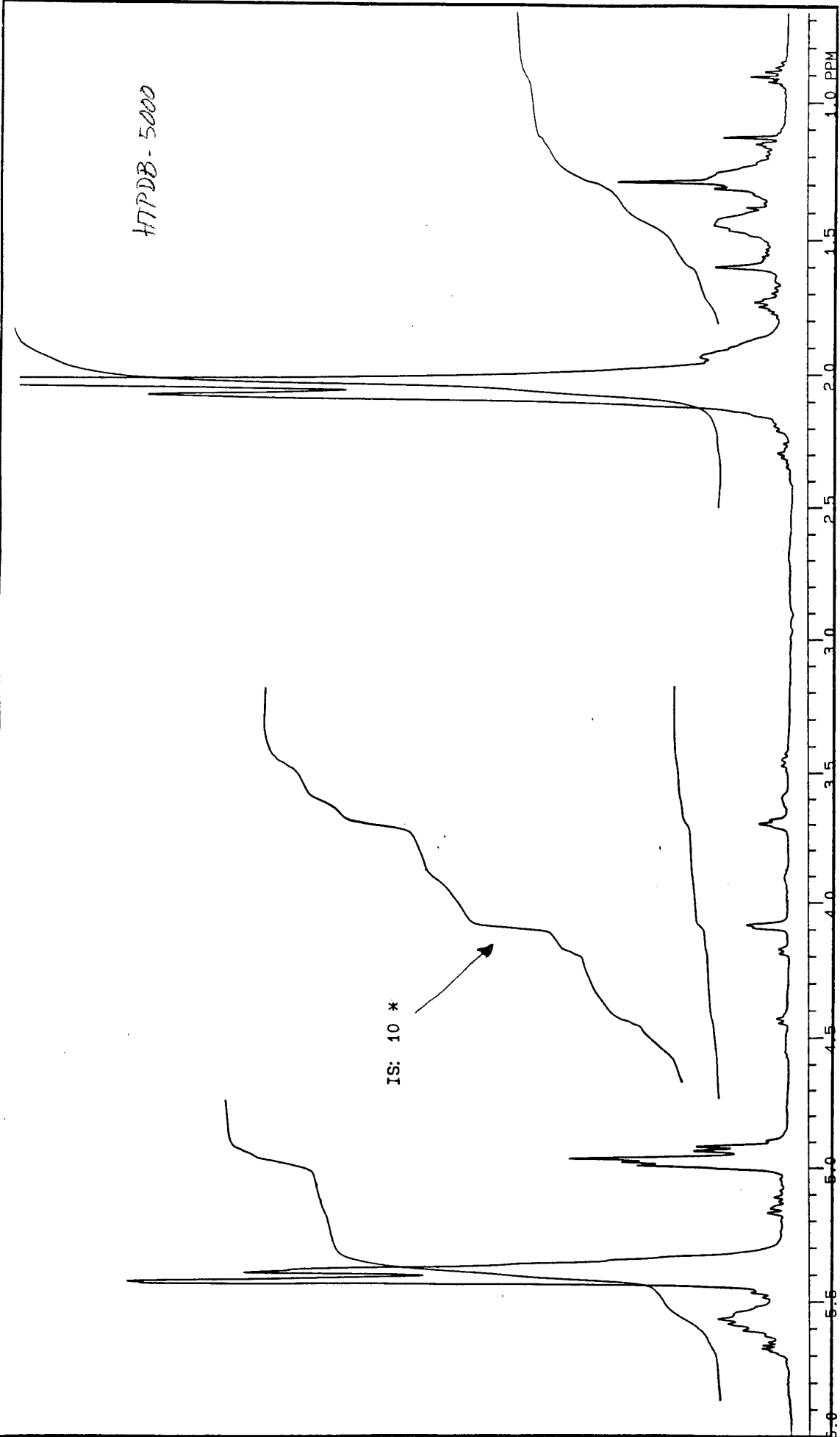
Pulse Sequence: STDHL
Tube OD: _____ mm
Temp: _____ °C
Solvent: CDCL3

EXPERIMENT
P1: 32.1 RE: _____ sec CD: _____ sec
L1: _____ Hz AF: _____ sec CD: _____
Width: 2132.5 Hz/gm Start: 269.9 Hz/gm
Reference: _____

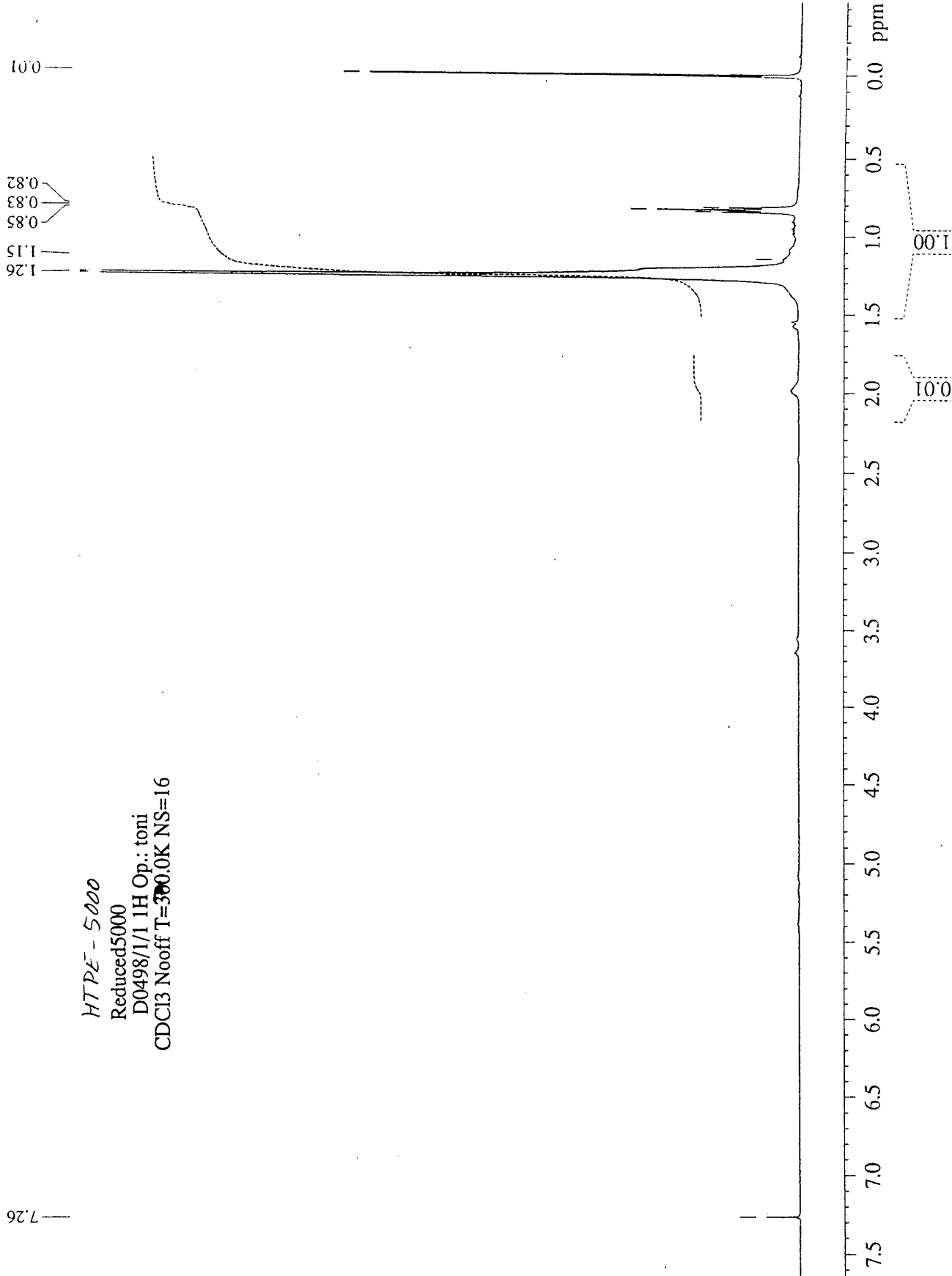
PLOT/PROCESSING
Nucleus: 1-1250 Other: 75-0 Hz
Mode: 1000 Power: 30 dB
Modulation Mode: C Freq: 300 Hz
Pulse Width: _____ μsec Power Mode: _____

DESCRIBE
Nucleus: 1-750 Freq: 400 MHz
Spec. Width: 9998.8 Hz Other: 174.0 Hz
Acq. Time: 3.995 sec Delay: 0 sec
Pulse Width: 7.0 μsec Transmits: 16

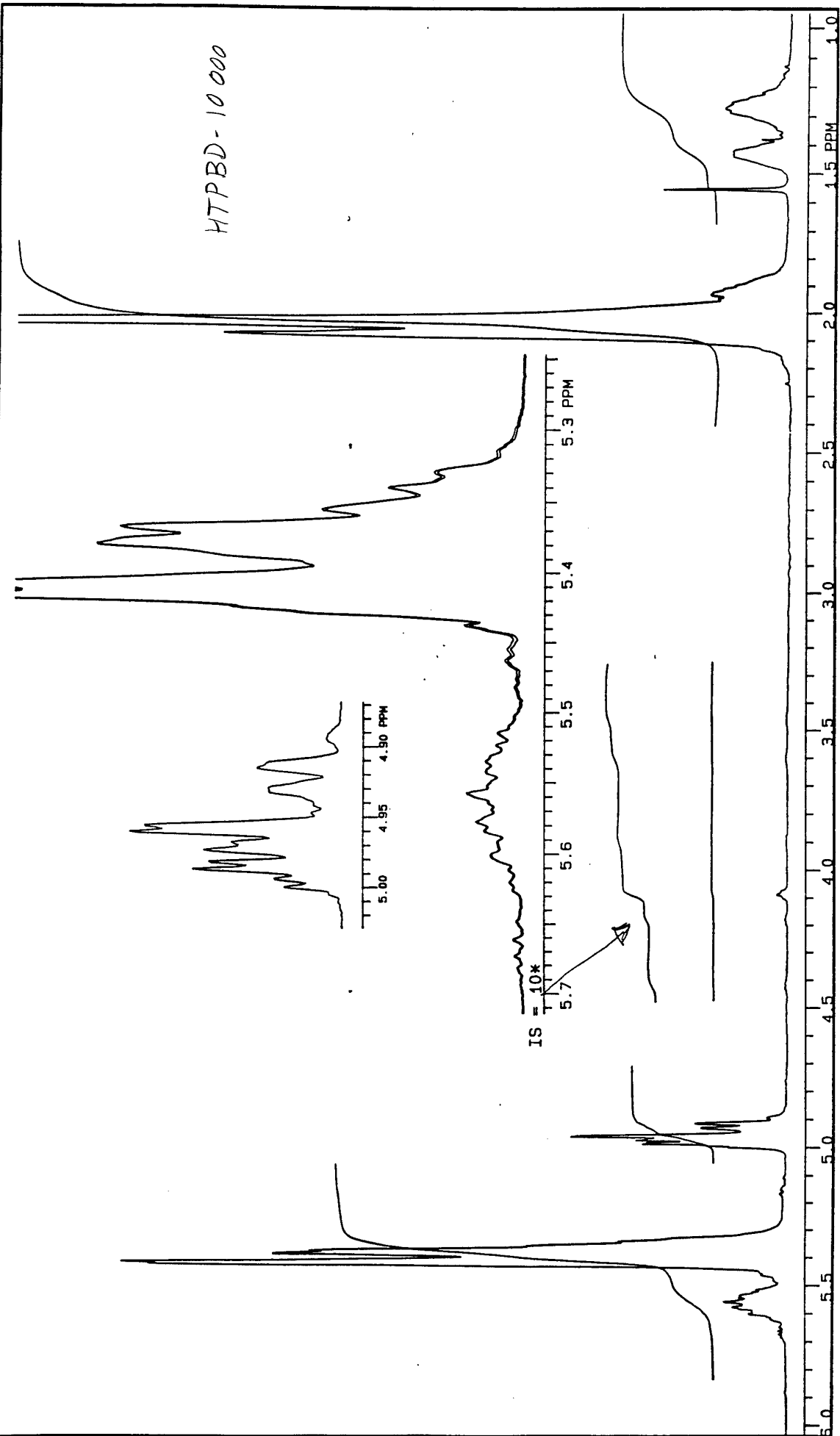
OSSEVE



HTPE - 5000
Reduced5000
D0498/1/1 1H Op.: toni
CDCI3 Nooff T=300.0K NS=16



HTPBD-10 000



Number _____
 File H
 Date 08-10-96
 XL YXR 400varian

SAMPLE
 H-9918 (21023)
 HTPBD-1E4 (CDCL3)
 KELLER F./S.E.
 Pulse Sequence SID1H
 Tube O.D. _____ mm
 Temp _____ °C
 Solvent CDCL3

EXPERIMENT
 FN 32 K RE sec CD _____ sec
 LB _____ Hz AF _____ sec CCD _____
 Width 2034.0 Hz/ppm Start 380.1 Hz/ppm
 Reference _____

PL01/PROCESSING
 Nucleus 1-750 Offset 75.0 Hz
 Mode NNN Power 20 db
 Modulation Mode C Freq 200 Hz
 Pulse Width _____ sec Power Mode _____

OBSERVE
 Nucleus 1-750 Freq 400 MHz
 Spec Width 5998.8 Hz Offset -174.8 Hz
 Acq Time 3.995 sec Delay 0 sec
 Pulse Width 7.0 sec Transmits 16



HTPE- 10.000
Reduced 10000
D0496/1/1 1H Op.: toni
CDC13 Nooff T=300.0K NS=32

