

1st Interim Report, Contract No. N68171-95-C-9105

Title: Isodisperse Telechelic Polymers and their Polyurethane Derivatives.

Sample preparation.

In the first part of the Contract, three HTPBD samples have been prepared, characterized by the following molecular weights:

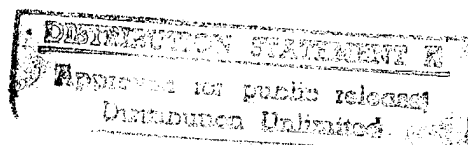
- | | |
|--------|---|
| No. 1. | Nominal: $\bar{M}_n = 3000$
Experimental: $\bar{M}_n = 3250$
Polydispersity: $\bar{M}_w/\bar{M}_n = 6460/3250 = 1.98$ |
| No. 2. | Nominal: $\bar{M}_n = 2000$
Experimental: $\bar{M}_n = 1870$
Polydispersity: $\bar{M}_w/\bar{M}_n = 3030/1870 = 1.62$ |
| No. 3. | Nominal: $\bar{M}_n = 5000$
Experimental: $\bar{M}_n = 5230$
Polydispersity: $\bar{M}_w/\bar{M}_n = 9022/5260 = 1.72$ |

Although the polydispersities of the samples are slightly different, they are within the limits given in our US Patent ($\bar{M}_w/\bar{M}_n = 1.5$ to 2.0). Due to the different molecular weights, every sample was prepared with a somewhat different polymerization recipe, the details were given in our previous 1st Interim Report (September 28, 1995, Contract No. N68171-95-C-9086). The No. 1. sample was handed personally by Prof. F. Tüdös to dr. G. Hagnauer on July 6, this year, in Watertown. The No. 2. and No. 3. samples were sent by air mail on October 13, this year. The structures of the samples were characterized by FT-IR, $^1\text{H-NMR}$ and GPC investigations. The measurements are given graphically, their evaluations are summarized in the Table 1.

The $^1\text{H-NMR}$ spectra of the samples were recorded by a Varian 400 type instrument.

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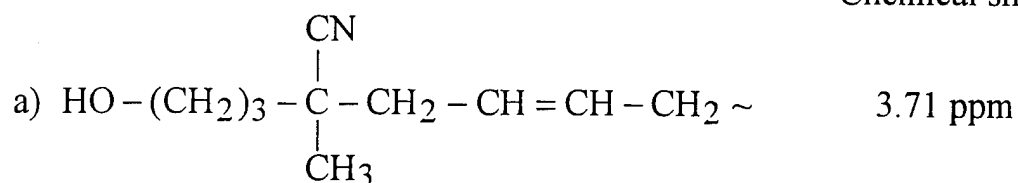
Figures 2-4 show the $^1\text{H-NMR}$ spectra of the samples HTPBD-2000, HTPBD-3000 and HTPBD-5000. All the three spectra consist of three regions. The aliphatic $-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2$ and $-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}_3$ protons appear at 1.0-2.2 ppm. The peaks appearing in the range 3.7-4.1 ppm correspond to the protons of $-\text{CH}_2-$ and $-\text{CH}$ groups adjacent to the chain-end $-\text{OH}$ groups. The peaks characteristic to protons of unsaturated $-\text{CH}=\text{CH}-$ and $-\text{CH}=\text{C}-$ groups formed from 1,4 and 1,2 linkages in the repeating units of polybutadiene appear at 4.9-5.5 ppm. The ratio of integrals of the peaks belonging to the protons of these both groups gives the ratio of butadiene units built in to the polymers with 1,2 and 1,4 linkages. According to the calculations, one 1,2 linkage falls to about five 1,4 linkages (see Table 1.).

Table 1. Microstructure of HTPBD samples based on FT-IR and $^1\text{H-NMR}$ measurements

Sample	Microstructure by					
	FT-IR (Fig.1.)			$^1\text{H-NMR}$		
	1,2 bond	1,4 bond cis	1,4 bond trans	1,2 bond	1,4 bond	Figure, HTPBD-
	%			%		
1	13	53	34	17.8	82.2	-3000
2	13	54	33	16.6	83.4	-2000
3	13	54	33	16.9	83.1	-5000

Owing to the combined initiation and to the combination of 1,2- and 1,4- units formed during chain propagation, the NMR can distinguish three OH structures at the chain-end:

Chemical shift:



Molecular weight distribution was estimated by gel permeation chromatography (GPC) method using Waters basic equipment: pump model 510, injector model U6K and a set of four chromatographic columns packed with crosslinked polystyrene gel, ("ultrastyrigel") of particle size less than 10 microns and pore size of 10E3, 10E2, 100 and 50nm. The molecular weight distributions are given graphically.

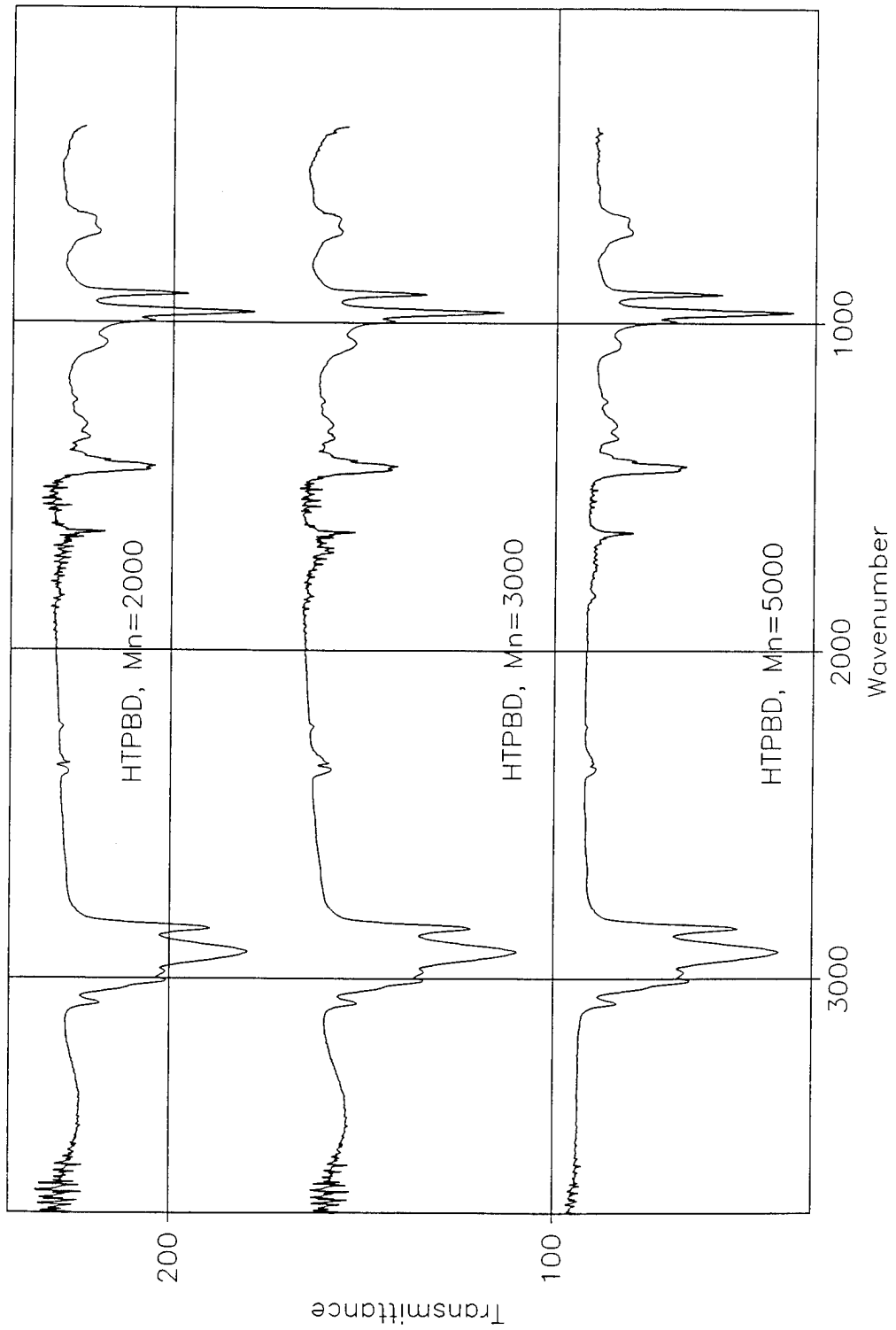
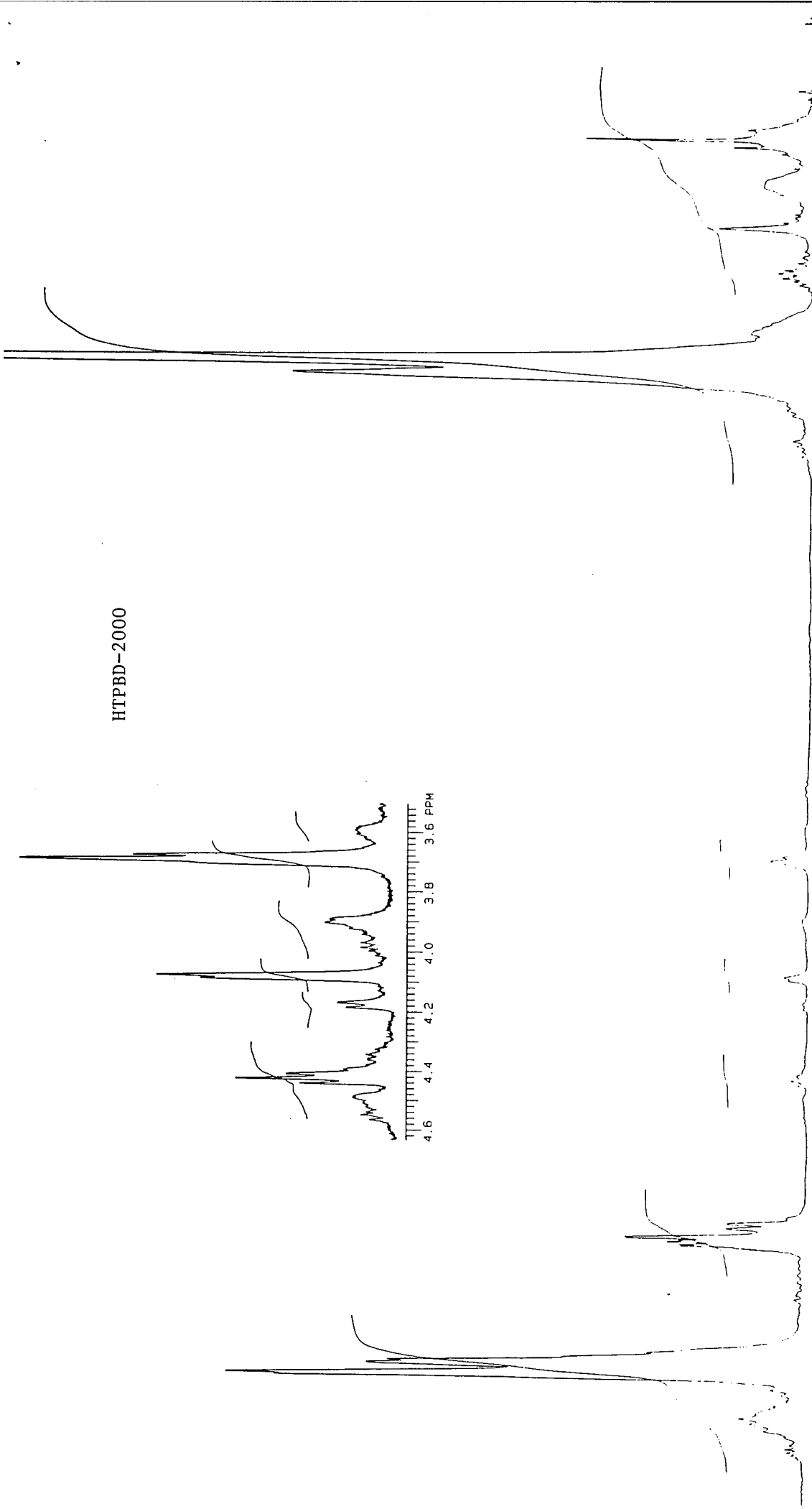


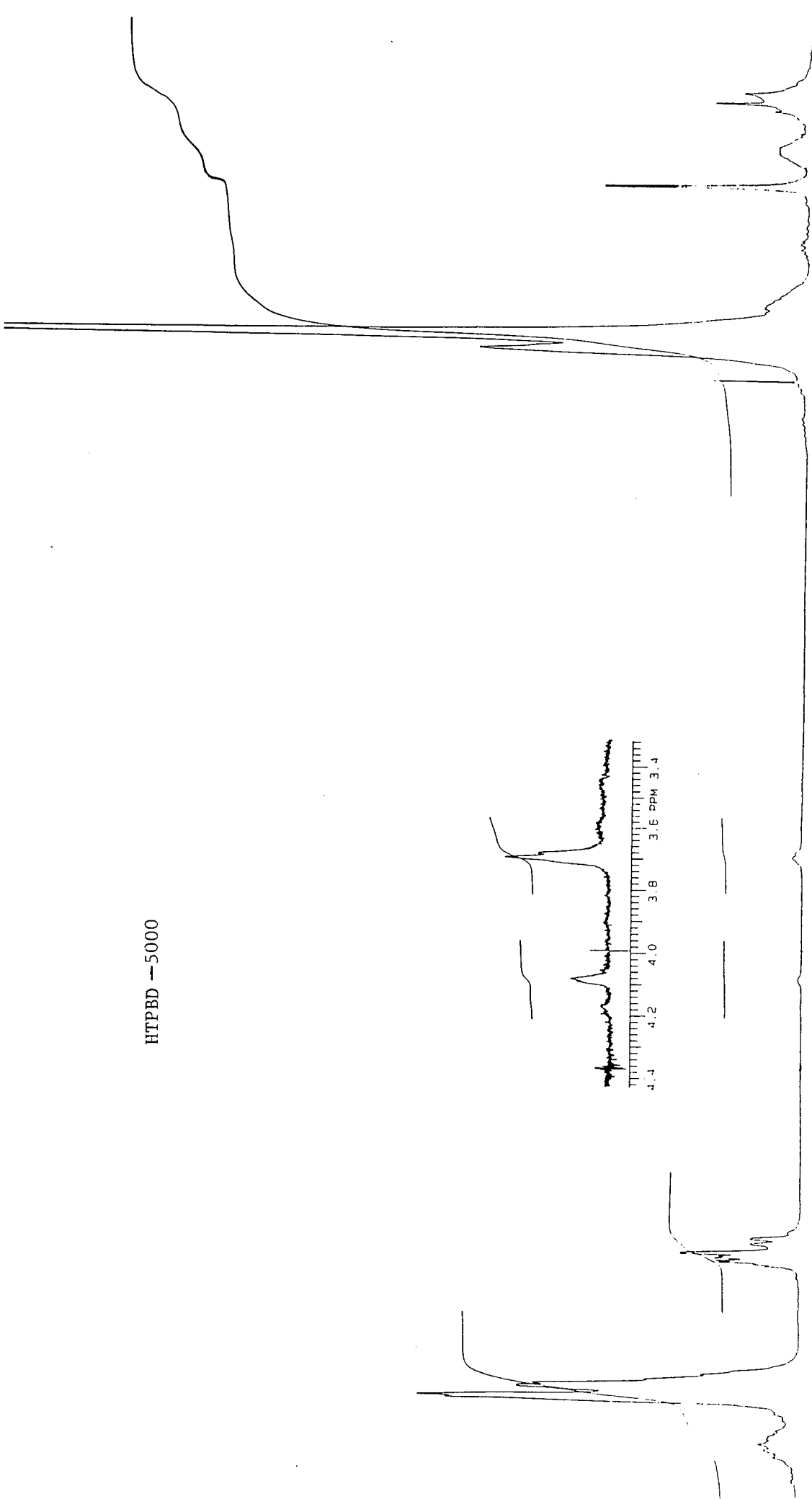
Figure 1. FT-IR spectra of polybutadiene diol samples.

HTPBD-2000



Nucleus	1.750	Freq	400	MHz	
Scan Width	5000.0	Hz	Offset	327.0	Hz
Acq Time	3.974	sec	Delay	0	sec
Pulse Width	7.0	μsec	Transmits	15	
Nucleus	1.750	Offset	75.0	Hz	
Mode	FHN	Power	20	db	
Modulation Mode	C	Freq	200	Hz	
Pulse Width		μsec	Power Mode		
FN	LB	RE	CD	sec	sec
Wath	3040.5	Hz	Start	319.8	Hz
Reference					
Pulse Sequence	STC:H				
Tube CD		mm			
Temp		°C			
Solvent	CDCL3				
EXPERIMENT					
SAMPLE	H-7378 (18600)				
	POLIBUTADIEN (CCCL3) 78u-124				
	KESLER B./E.O.				
Number	HBE162				
File	13-09-95				
Date					
XL	VXR 400				

HTPBD -5000

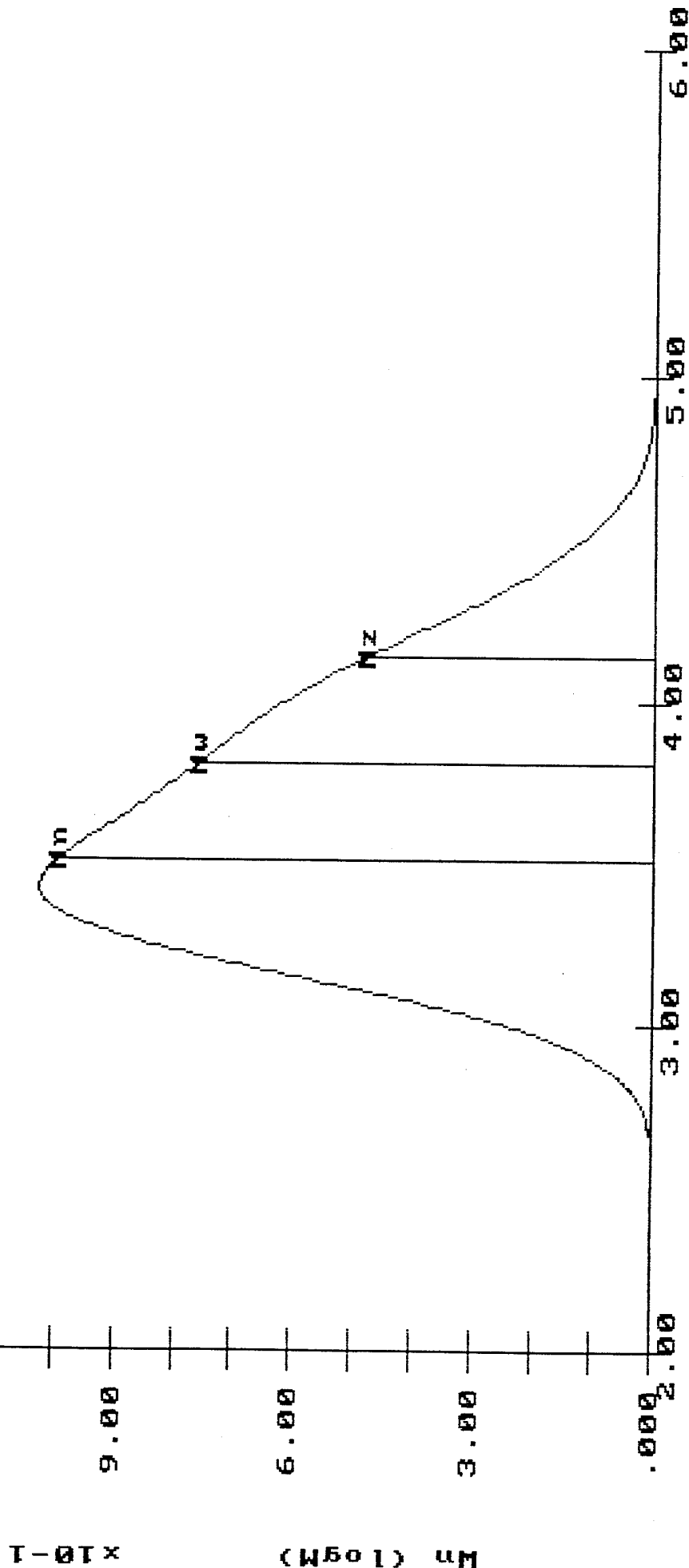


Nucleus	1.750	Freq	400	MHz	
Spec Width	5000.0	Hz	Offset	-174.8	Hz
Acq Time	4.000	sec	Delay	0	sec
Pulse Width	7.0	µsec	Transmits	16	
Magnus	1.750	Mode	1MIN	Modulation Mode	C
Offset	75.0	Hz	Power	20	db
Freq	200	Hz	Power Mode		
Reference					
FN	32	K	RE		sec
CD					sec
LB		Hz	AF		sec
CCD					sec
Width	1947.1	Hz	Start	372.3	Hz
EXPERIMENT					
Pulse Sequence	STJ1H				
Tube OD		mm			
Temp		°C			
Solvent	CDCL3				
SAMPLE					
H-7412	(18600)				
PBU-126	(CDCL3)				
KESLER B. E. O.					
Number	K226H				
File	14-09-95				
Date					
VXR	400	VBT			

VISCOTEK CORP. UCAL 4.05 ENDED: 06/14/95 13:52
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Mw = 6.45E3
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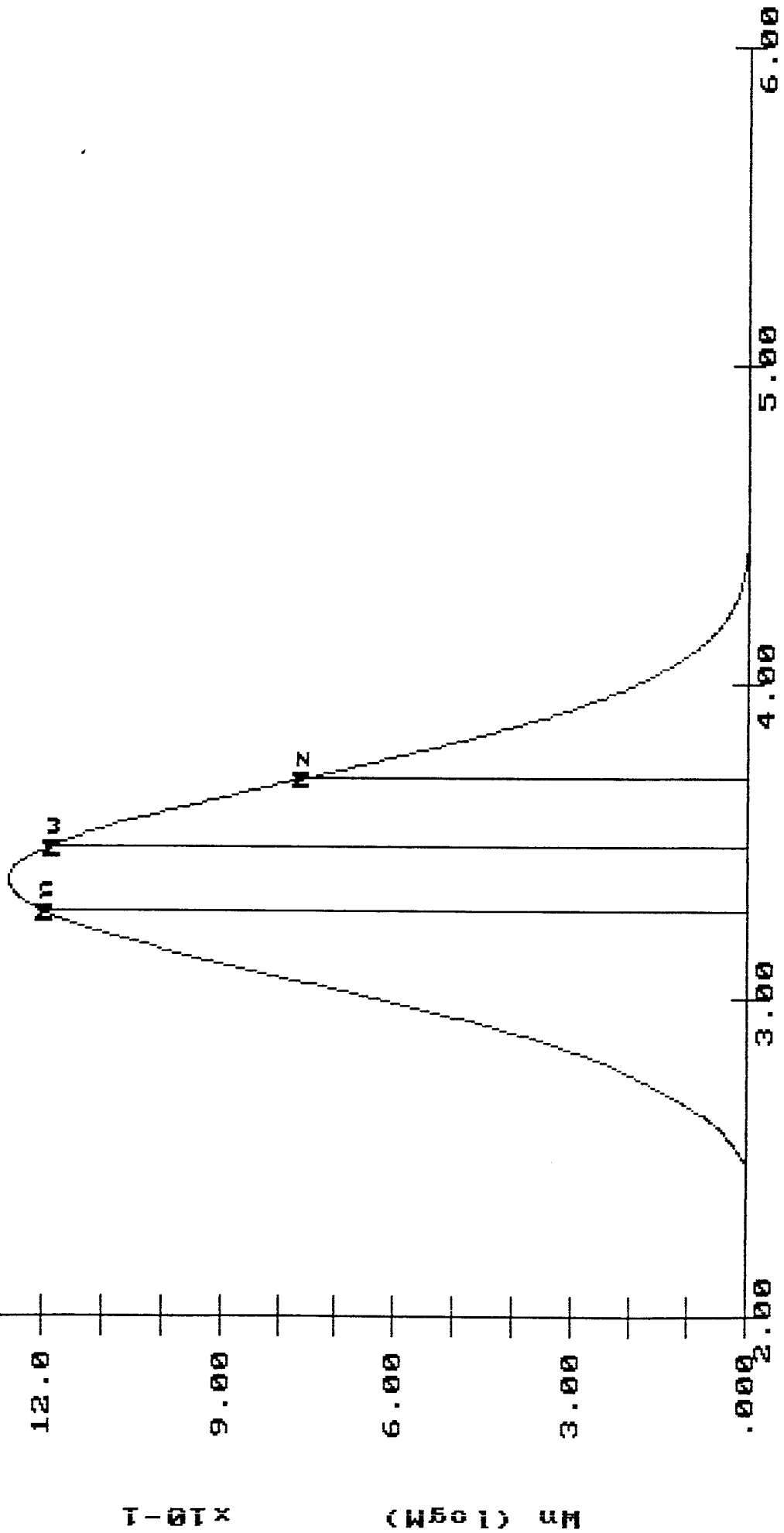
MOLECULAR WEIGHT DISTRIBUTION



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

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VISCOOTEK CORP.

UCAL 4.05

ENDED: 10/05/95

15:02

FILENAME: 5Ka

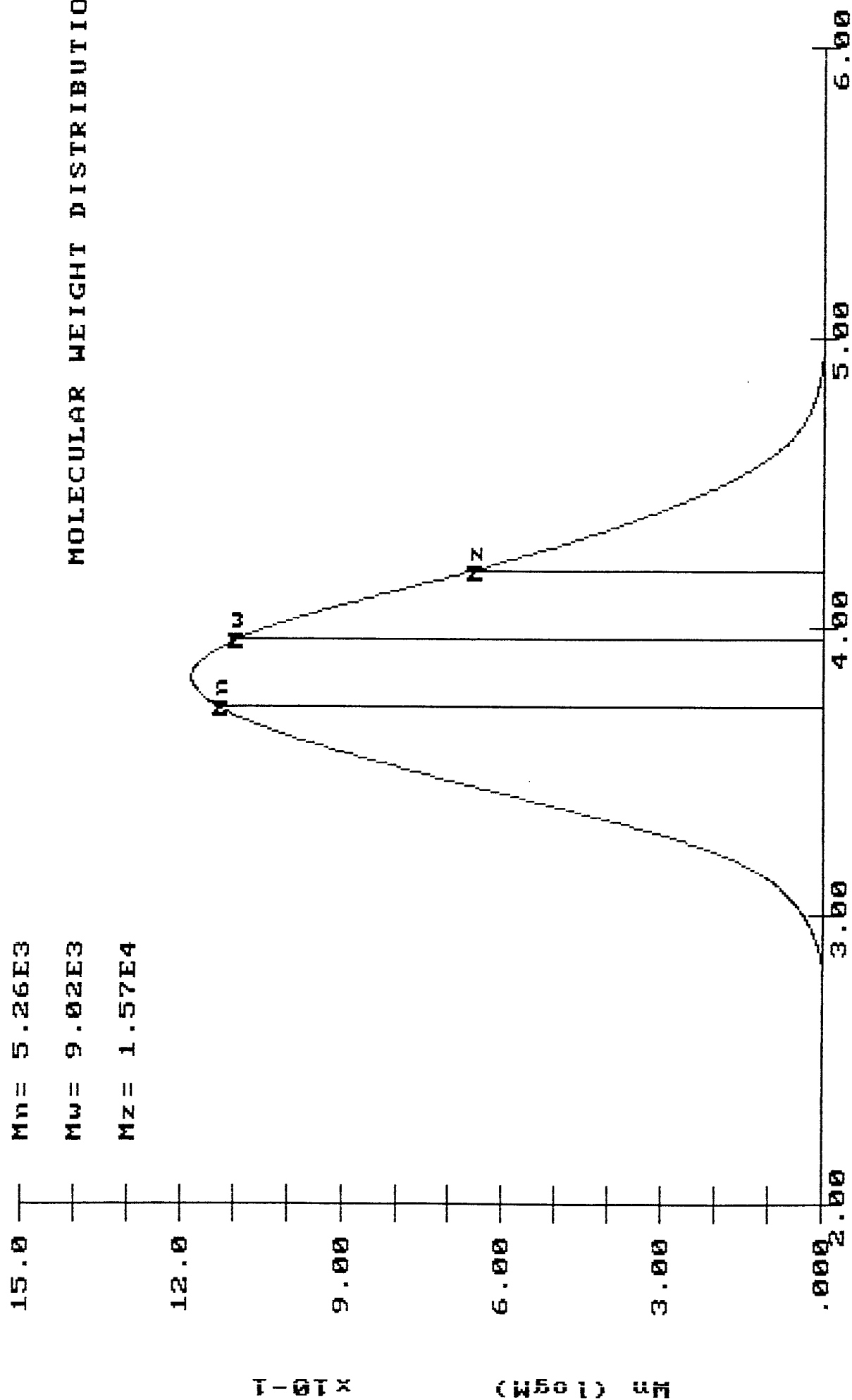
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Mw = 9.02E3

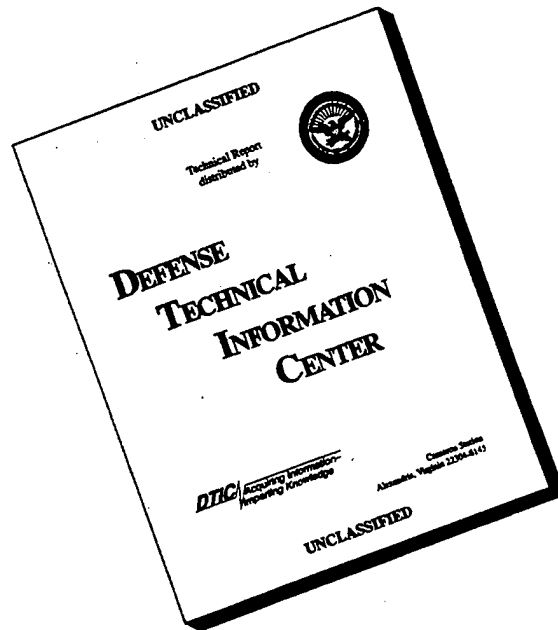
Mz = 1.57E4

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