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2nd Interim Report, Contract N 68171-95-C-9086

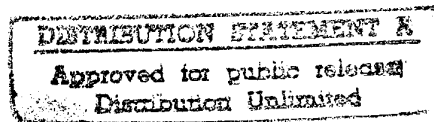
Title: Isodisperse Telechelic Polymers and their Polyurethane Derivatives

In this part of the Contract three other HTPBD samples have been prepared, characterised by the following molecular weights:

No.4. Nominal $\bar{M}_n = 1000$
Experimental: $\bar{M}_n = 1245$
Polydispersity: $\bar{M}_w/\bar{M}_n = 1,34$

No.5. Nominal $\bar{M}_n = 1500$
Experimental: $\bar{M}_n = 1552$
Polydispersity: $\bar{M}_w/\bar{M}_n = 1,34$

No.6. Nominal $\bar{M}_n = 10000$
Experimental: $\bar{M}_n = 10800$
Polydispersity: $\bar{M}_w/\bar{M}_n = 1,95$



The details of the polymerization recipe of the individual samples were given in our previous 2nd Interim Report (December 21, 1995. Contract No. N68171-95-C-9086). The samples were sent by air mail on January 25, 1996. The structures of the samples were characterised by FT-IR, $^1\text{H-NMR}$ and GPC investigations. The measurements are given graphically, their evaluations are summarised in the Table 1.

The FT-IR spectra of the samples were recorded by a Bomem MB-100 spectrophotometer. Figure 1 shows the FT-IR spectra of the samples HTPBD-1000, HTPBD-1500 and HTPBD-10000.

The percentage of the 1,4-trans, 1,2-, and 1,4-cis-linkages in the polybutadiene chain was calculated from the respective absorption at

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965.7 cm^{-1} , 911.7 cm^{-1} and 722.7 cm^{-1} . We have to emphasise that the weak absorption of the 1,4-cis units at 720-740 cm^{-1} can cause some uncertainty in the calculation.

The three spectra show difference only in two regions. Because of the high molecular weight of the HTPBD-10000 the OH endgroup concentration is very low and their absorption at 3200-3600 cm^{-1} can not be seen. For the same reason the absorption of the $-\text{C}\equiv\text{N}$ group of the initiator fragments at 2218.7 cm^{-1} appears only in the spectra of the HTPBD-1000 and HTPBD-1500. In case of these polymers the intensity of the absorption of the $-\text{OH}$ and $-\text{C}\equiv\text{N}$ groups is also effected by the respective groups of the recombination product of the ACP initiator remained in the polymers.

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

Sample	Microstructure by				
	FT-IR			$^1\text{H-NMR}$	
	1,2 bond	1,4 bond cis	1,4 bond trans	1,2 bond	1,4 bond
	%			%	
HTPBD-1000	11.1	35.2	53.6	14.7	85.3
HTPBD-1500	11.1	31.0	57.9	14.7	85.3
HTPBD-10000	12.6	28.3	59.2	14.0	86

The microstructure of the polymers determined by the FT-IR measurements were verified by the data based on the $^1\text{H-NMR}$ measurements (see Table 1).

Figures 2-4 show the $^1\text{H-NMR}$ spectra of the samples. The assignment of the peaks were given in our 1st Interim Report (November 10, 1995.) Since HTPBD-1000 and HTPBD-1500 were synthesised using only ACP initiator the resonance at 4.08 ppm correlated to the protons in the $\text{HO-CH}_2\text{-CH=CH-CH}_2\text{-group}$ (end group in case of H_2O_2 -initiation) can not be seen in the spectra of the polymers above.

Figures 5-7 show the molecular weight distribution of the three polymers. It is noteworthy that the molecular weight distribution of samples No.4 and No.5 is lower even than the theoretical value ($\overline{M}_w/\overline{M}_n = 1.5$). This is favourable in respect of the physical-mechanical properties of the PU rubbers prepared with these samples since oligomers with mono dispersity would give the best rubber according to the elasticity theory.

At the same time the question arises that what would be the interpretation of the polydispersity lower than the theoretical one.

We have two explanations, an experimental and a theoretical one.

According to the experimental explanation the calibration curve of the GPC is inaccurate in the low molecular weight range ($M_n < 1000$). Thus, the molecular weight distribution calculated by means of such calibration curve will be inaccurate to the same extent as the calibration curve itself. So, the cause of the deviation according to this assumption is the imperfectness in the evaluation of the calibration curve. A further possible explanation is that during the samples preparation the very low molecular weight portion of the polymer is partially lost causing narrowing of the molecular weight distribution.

The theoretical explanation is based on the fundamental of the distribution functions. Strictly speaking, the rate constants of the elemental reactions in the polymerization are size-dependent:



or



where $R \cdot$ stands for the growing active center and P for the polymer molecule formed.

That is the numerical value of $k_{2,i}$ and $k_{4,ij}$ depends on the size of $R_i \cdot$ and $R_j \cdot$ (practically the degree of the polymerization).

As a reminder: according to the collision theory (the simplest reaction kinetic theory) the collision number (z) (that is the preexponential coefficient of the rate constant) is the function of the molecular weight of the reaction partners.

In the today practice we assume that $k_{2,i}$ and $k_{4,ij}$ is independent of the size (molecular weight) of the active center:

$$k_{2,i} = k_2 = \text{const.} \quad (3)$$

$$k_{4,ij} = k_4 = \text{const.} \quad (4)$$

However, we must keep in mind that the above assumption serving our convenience during the calculation is not valid under any circumstances like a theoretical thesis.

Research in the past decades primarily on the field of telomerization has proved that in the low molecular weight range:

$$1 \leq i, j \leq 20 \quad (5)$$

the above assumption is applicable only with restriction or not at all since the experimental results deviate considerably from the distribution functions calculated by the theory.

To determine which explanation is valid in our case, more designed experimental work must be done. This work may be accomplished during our planned cooperation in 1996.

At this point we can conclude that the lower molecular weight distribution is even favourable for the preparation of the PU rubbers.

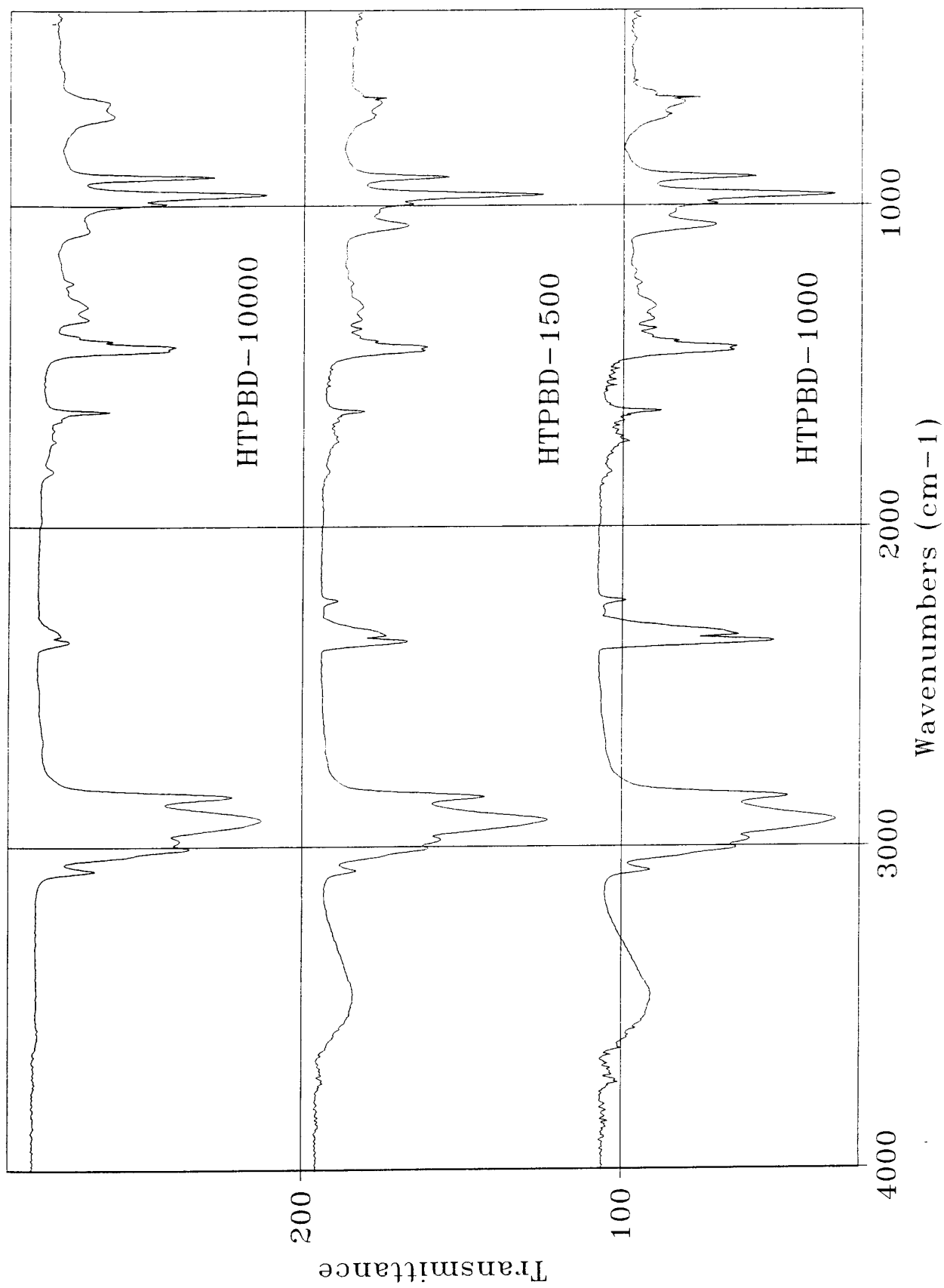


Figure 1. FT-IR Spectra of HTPBD samples.

Figure 2. ¹H-NMR spectrum of HTPBD-1000

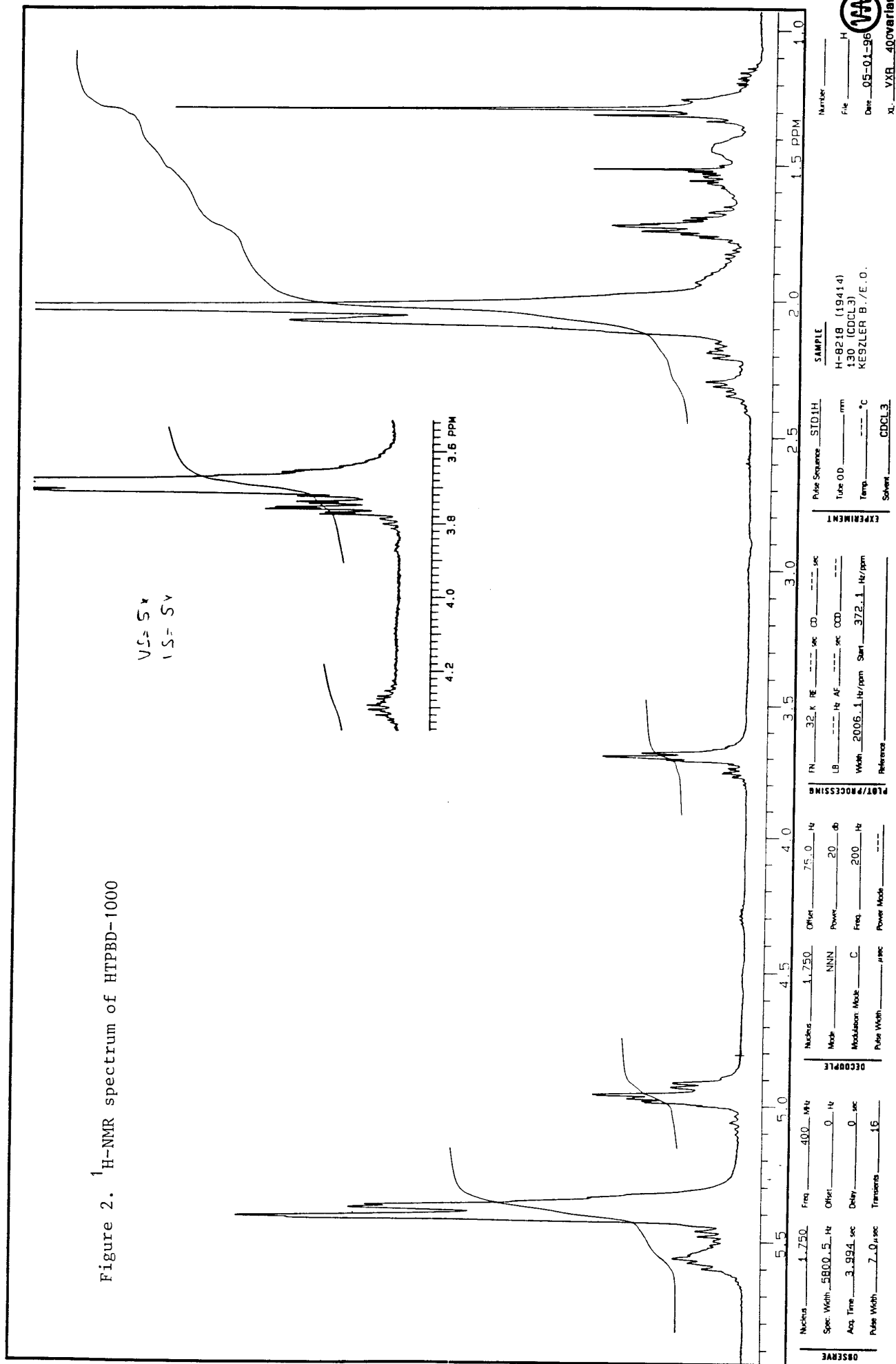
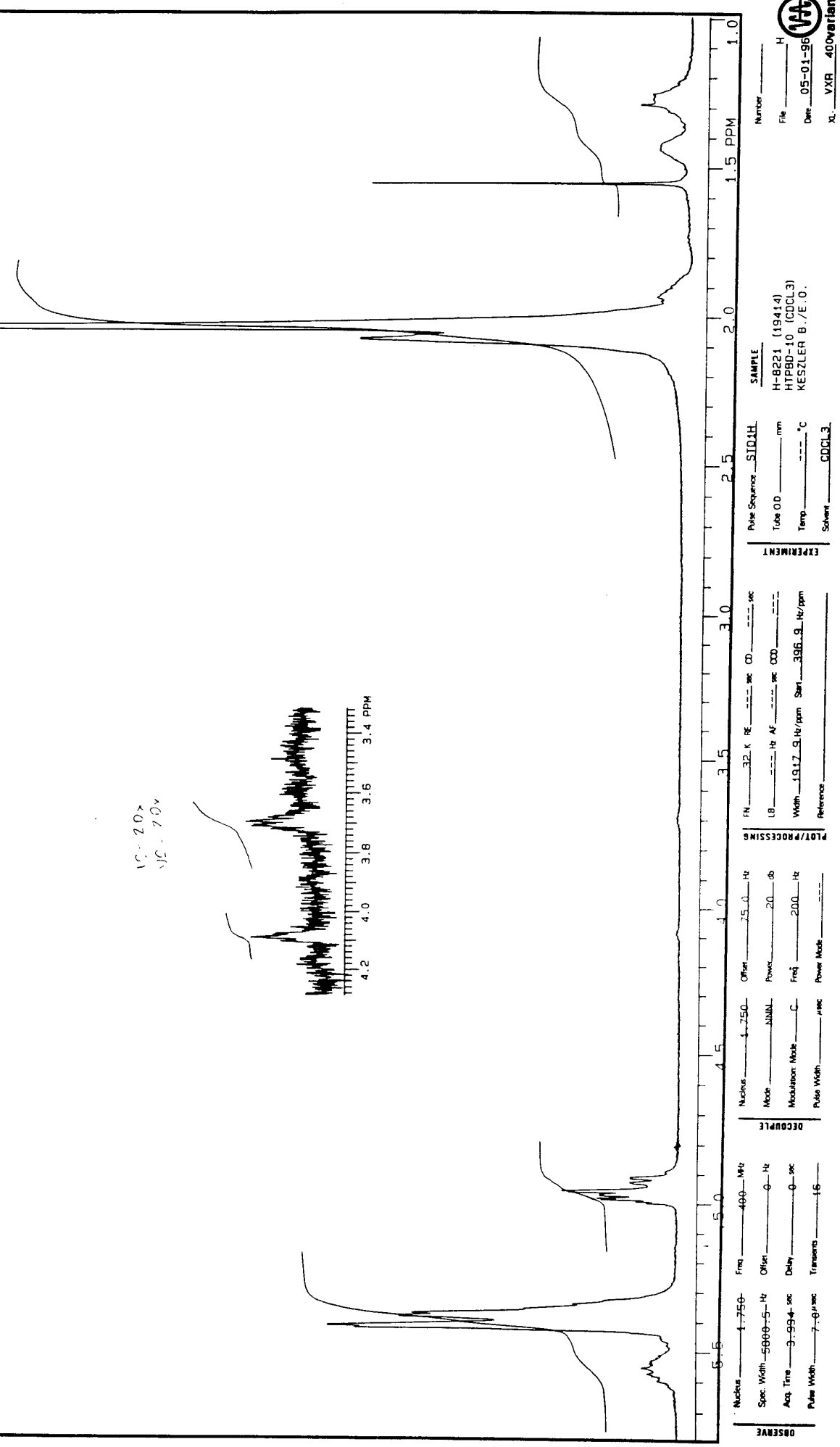


Figure 4. ¹H-NMR spectrum of HTPBD-10000



10. 2.0x
10. 70x

OSERVE

Nucleus 1H Freq 400 MHz

Spec. Width 5000 Hz Offset 0 Hz

Acq. Time 3.994 sec Delay 0 sec

Pulse Width 7.0 μ sec Transmits 16

DECUPLE

Nucleus 1H Mode NOVA Modulation Mode C Pulse Width AVC

Offset 75.0 Hz Power 20 dB Freq 200 Hz

PLT/PROCESSING

FN 32 K RE --- sec CD --- sec

LB --- Hz AF --- sec CD --- sec

Width 1917.9 Hz/ppm Start 396.9 Hz/ppm

Reference ---

EXPERIMENT

Pulse Sequence SID1H

Tube OD --- 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

VISCOTEK CORP. UCAL 4.05 ENDED: 12/07/95 16:44
FILENAME: 1372aa RUN ID: 95/325 Polibut. 137/2

MOLECULAR WEIGHT DISTRIBUTION

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

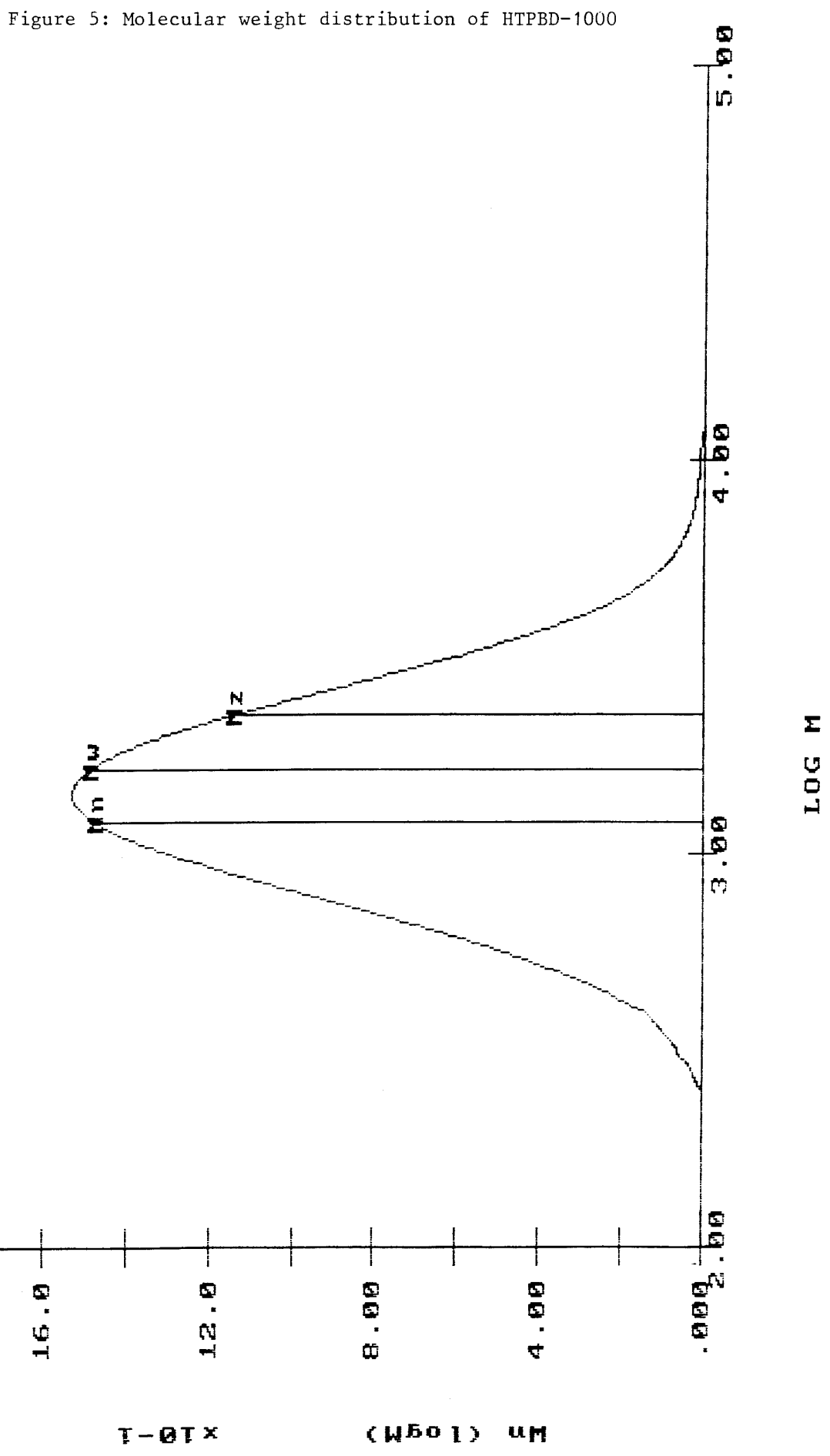


Figure 5: Molecular weight distribution of HTPBD-1000

VISCO TEK CORP. UCAL 4.05 ENDED: 11/16/95 15:26
 FILENAME: 13044aa RUN ID: 95/303 Polibut.130/44a

Mn = 1.53E3
 Mw = 2.07E3
 Mz = 2.84E3

MOLECULAR WEIGHT DISTRIBUTION

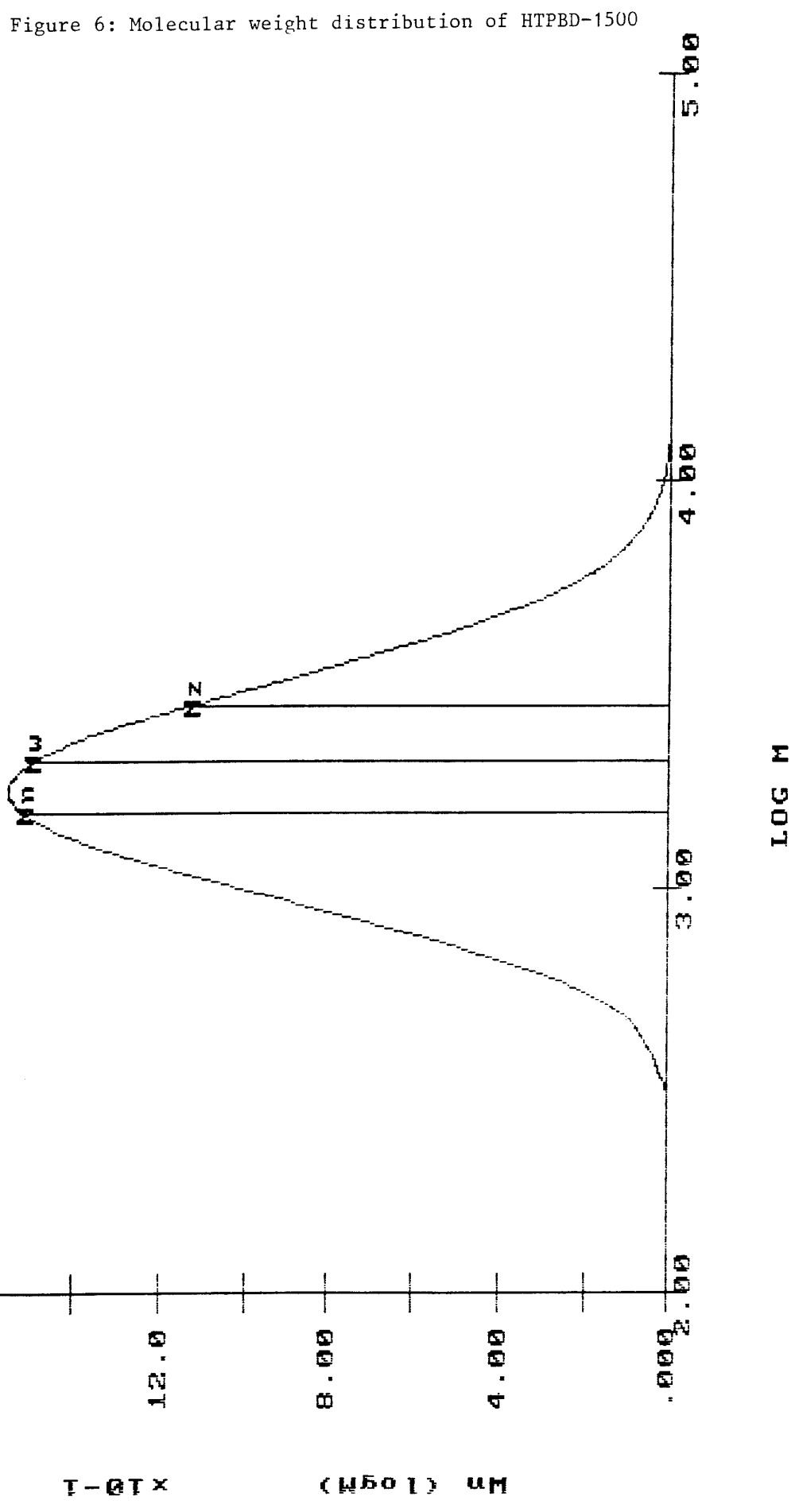


Figure 6: Molecular weight distribution of HTPBD-1500

VISCOUSER CURF. UCHL 4.00 ENDED: 01/03/96 14:06
FILENAME: x6a RUN ID: 96/1 polibut. X-6

Mn = 1.08E4
Mw = 2.10E4
Mz = 3.78E4

MOLECULAR WEIGHT DISTRIBUTION

Figure 7: Molecular weight distribution of HTPBD-10000

