

Isodisperse Telechelic Polymers and their Polyurethane Derivatives

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by

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Abstracts

This report describes the so-called "isodisperse telechelic polymerization" method for the preparation of hydroxy-terminated polybutadienes (HTPBD). From these polymer diols polyurethane can be produced.

This method relates to a process for preparing (co)polymers, with polydispersity approaching the theoretical polydispersity and with functional groups in α,ω -positions by radical (co)polymerization of radically polymerizable monomer(s), using one or more initiators.

The isodisperse polymerization can be approximately realized by isothermal polymerization but with very rigid polymerization regime. The exact isodisperse polymerization regime can be realized under nonisothermal conditions. For the practical realization of the method, the degree of polymerization is regulated by the continuous elevation of the temperature according to a "temperature program" determined by a function describing the variation of the polymerization process against time with the aid of independent variables affecting the process (concentrations, initial temperature, etc.). A brief description of the polymerization recipe is given for the preparation of HTPBD samples with $\overline{M}_n = 1000; 1500; 2000; 3000; 5000$ and 10 000. We characterized the samples by FT-IR, $^1\text{H-NMR}$ and GPC methods.

For the isodisperse polymerization, we calculated (i) the limiting conversion of polymerization and (ii) the initial temperature of polymerization. Finally, we analyzed the function of the temperature program.

Keywords: isodisperse telechelic polymerization, hydroxy-terminated polybutadienes, polyurethane, polydispersity, functional groups, isothermal polymerization, nonisothermal conditions, degree of polymerization, temperature program, limiting conversion of polymerization, initial temperature of polymerization

Table of Contents

Title Page	1
Abstracts	2
Table of Contents	3
1. § Introduction	4
2. § The isodisperse telechelic polymerization	6
A.) General considerations	6
B.) Isothermal case	9
C.) Non-isothermal case	11
D.) The practical realization of the method	13
3. § Experimental	16
4. § Results and Discussion	20
5. § Further theoretical problems	30
A.) Determination of the limiting conversion of isodisperse polymerization	30
B.) Calculation of initial temperature of isodisperse polymerization	33
C.) Analysis of the function of the temperature program	33
References	37
Figures 4-12	38

1. § Introduction

In recent years great interest has been shown towards hydroxy telechelic polymers with designed low molecular weight and narrow polydispersity. The applications of these telechelic polymers may be divided into the following groups:

- direct incorporation into a polymeric matrix to alter the physical properties such as viscosity, tack, etc. Liquid polymers like hydroxytelechelic polybutadienes (HTPB), especially butadiene-acrylonitrile copolymers are useful as tackifier for rubbers and acrylic coatings and increase the viscosity of synthetic or mineral oils (1, 2).
- chemical modification reactive sites (chain ends, double bonds in the chain, etc.) before the use of the polymers as additive, adhesive, catalyst support, etc. The hydroxyl end groups can be converted into acrylic, ester, acid or acid chloride groups (3, 4). Utilizing the acrylic end groups thermoplastic butadiene-acrylate or butadiene-styrene elastomers can be synthesized. Similarly to other adhesives (meth)acryl terminated polymers can be crosslinked with peroxides or by UV irradiation (5). Increased flexibility, heat, ozone and hydrolytic resistance, as well as improved modulus and strength of the adhesives are the characteristic effect of such modification on properties. Hydrogenated HTPBs used in the propellant field (6, 7), as lubricating oil additives, plasticisers, but also as catalyst support in the ethylene polymerization (8).
- crosslinking with multifunctional reagents to obtain macromolecular networks. The most important of these reactions concerns the condensation of liquid hydroxytelechelic polydienes with isocyanates. The

addition product are used as solid propellant binders (9). Crosslinked product reinforced with carbon black can be used in the tire industry.

Besides some particular cases such as ozonolysis (10), or ring-opening polymerization of ketene-acetal type monomers (11), the hydroxy telechelic polymers can be synthesized also by anionic polymerization resulting polymers with small polydispersity and theoretical functionality of two (12). The free-radical polymerization is also suitable and probably the most cost-effective method for making such polymers disubstituted by functional groups in α, ω -positions (13, 14). The functionality of the polymer formed is determined in each case by the incorporated initiating radicals carrying the functional group. However, in radical polymerization it is a difficult task to assure appropriate polydispersity ($=P_w/P_n$). This is partly due to decrease in the initiator concentration during the reaction involving in the deceleration of the radical producing process, (i.e. the rate of initiation gradually decreases). The other reason is the decrease in concentration of the monomer and the possible gel-effect. The simultaneous decrease in the concentration of the monomer (to smaller extent) and of the initiator (to higher extent) causes a change in the degree of the polymerization together with that in polydispersity.

Recently, a research team of the Macromolecular Chemistry Department of CRIC elaborated a free-radical polymerization method of preparing α, ω -dihydroxy oligomers (telechelic oligomers) for the production of polyurethane elastomers (15). This method, the so-called isodisperse telechelic polymerization, makes it possible by elimination of the disadvantages of earlier attempts that M_n and M_w values of the telechelic polymers formed

(correspondingly, the P_n and P_w values) remain constant during the course of the polymerization, at any conversion. Correspondingly, the value of polydispersity, ($P.D. = P_w/P_n$) is kept at a minimum and constant value as well (so-called "isodisperse" polymerization). Theoretically, in the case of re-combination, $P.D. = 1.5$ and $F = 2$, in case of disproportionation $P.D. = 2.0$ and $F = 1$. The functionality of the oligomer (F) is also kept constant (usually, $F = 2 \pm 0.05$).

The Watertown Polymer Laboratory is interested in obtaining polyurethane elastomers having optimal physico-mechanical properties. According to the physico-chemical theory of elasticity, this goal can be reached by the use of isodisperse telechelic polymers. This Report concerns the synthesis of six hydroxy-terminated polybutadiene (HTPB) with molecular weights (M_n) of 1000, 1500, 2000, 3000, 5000 and 10000, one hundred gram of each. The theoretical aspects of the problem was investigated and the polymerization conditions of the HTPBs were elaborated. The microstructure of the samples were studied by GPC, FT-IR and 1H -NMR. The functionality (F) of the samples was also determined.

2. § The isodisperse telechelic polymerization

This method relates to a process for preparing (co)polymers, with polydispersity optionally approaching the theoretical polydispersity and with functional groups in α,ω -positions, by radical (co)polymerization of radically polymerizable monomer(s), using one or more initiators.

Radical polymerization for making polymers disubstituted by functional groups in α, ω -positions is performed according to the known methods by polymerizing the polymerization solution containing monomer or monomers, initiator and solvent at a given temperature for a given period of time. The functionality of the polymer formed is determined in each case by the incorporated initiating radicals carrying the functional group.

The aim of the present method is, by the elimination of the disadvantages of earlier attempts, to create a process which makes possible to produce polymers with optimal degree of polymerization and with polydispersity optionally approaching the theoretical polydispersity, by radical homo- and copolymerization.

The problem of minimum polydispersity in radical polymerization can be treated quantitatively as follows.

A.) General considerations

The value of \bar{P}_n is

a) in the case of disproportionation

$$\bar{P}_n = \frac{1}{1-\alpha} = \frac{k_2 m}{k_4 r} = \frac{1}{\kappa} \quad (2.1)$$

b) in the case of recombination

$$\bar{P}_n = \frac{2}{1-\alpha} = 2 \frac{k_2 m}{k_4 r} = \frac{2}{\kappa} \quad (2.2)$$

where k_2 and k_4 are the rate constants of propagation and termination, m and r are the concentration of monomer and radical, respectively, and α is the probability of chain propagation.

The momentary value of the polydispersity under the given conditions is:

a) disproportionation

$$\bar{P}_w / \bar{P}_n = 1 + \alpha \cong 2 \quad (2.3)$$

b) recombination

$$\bar{P}_w / \bar{P}_n = 1 + \frac{\alpha}{2} \cong 1,5 \quad (2.4)$$

In radical polymerization, this is the lowest polydispersity theoretically possible.

As is known, the definition of α is:

$$\alpha = \frac{k_2 m}{k_2 m + k_4 r^2} = \frac{k_2 m}{k_2 m + k_4 r} = \frac{1}{1 + \frac{k_4 r}{k_2 m}} = \frac{1}{1 + \kappa} = \text{const} \quad (2.5)$$

From Equ (2.5) it is obvious that the constancy of α can be assured only if the following condition is fulfilled:

$$\kappa = \frac{k_4 r}{k_2 m} = \text{const} \quad (2.6)$$

In steady state:

$$\kappa = \frac{k_4 r}{k_2 m} = \frac{k_4}{k_2 m} \sqrt{\frac{W_1}{k_4}} = \frac{\sqrt{W_1 k_4}}{k_2 m} \quad (2.7)$$

where $W_1 = 2k_1 f x$ is the rate of initiation, k_1 is the rate constant of decomposition of initiator, f is the radical efficiency factor and x is the concentration of initiator.

B.) Isothermal case

If it can be assured that no gel effect takes place up to the given limiting conversion

$$\xi_{\text{limit}} = \frac{\Delta m_{\text{limit}}}{m_0} \leq 0.6 \div 0.8 \quad (2.8)$$

i.e. the value of k_4 does not decrease (this condition is generally fulfilled for k_2 up to the given limiting conversion), then the condition $\kappa = \text{const}$ reduces to the simpler one:

$$\frac{\sqrt{x}}{m} = \kappa' = \text{const} \quad (2.9)$$

under isothermal conditions. A more detailed calculation shows, that this condition is fulfilled - in good approximation - at the initiator concentration:

$$x'_0 = \frac{k_1 k_4}{2f(2k_2)^2} = \frac{k_1}{8f} \delta^2 \quad (2.10)$$

where $\delta = \sqrt{k_4}/k_2$.

This condition seems feasible in some cases. The question is, whether the value of x'_0 can assure an acceptable rate of polymerization?

It is obvious that x'_0 depends on the temperature. If the temperature dependence of i -th elementary reaction is given by $k_i = A_i \exp\{-E_i/RT\}$, then

$$x'_0 = \frac{1}{8f} \frac{A_1 A_4}{A_2^2} \exp\left\{\frac{-1}{RT}(E_1 + E_4 - 2E_2)\right\} \quad (2.11)$$

In the case of usual activation energies

$$E_1 + E_4 > 2E_2 \quad (2.12)$$

More exactly, $\Delta E \approx 18 \div 36$ kcal/mol.

Thus, in such a case the value of x'_0 increases with the increase of temperature. So, there exists such a temperature at which a sufficient polymerization rate can be produced at a physically rational x'_0 value.

Simultaneously, the condition relating to \bar{P}_n should be kept too:

$$\kappa = \frac{1}{\bar{P}_n} = \frac{\sqrt{W_1 k_4}}{k_2 m} = \frac{\sqrt{2 k_1 f x_0 k_4}}{k_2 m_0} \quad (2.13)$$

If $x_0 = x'_0$ than

$$\kappa = \frac{k_1 k_4}{2 m_0 k_2^2} = \frac{k_1}{2 m_0} \delta^2 \quad (2.14)$$

Since the value of m_0 can be varied in a narrow range only, because it is determined by other aspects (e.g. productivity, solubility, exclusion of gel effect, etc.), we have only two "free" parameters for a given monomer,

- a) the nature of the initiator (k_1) and
- b) the temperature.

These two parameters should be chosen so that the required value of \bar{P}_n (or κ) be kept for the whole period of reaction.

Although this analysis shows that the condition (2.6) is feasible in good approximation under isothermal conditions at a certain combination of initial concentrations, the technological conditions (2.10) are extremely rigid and in some cases they can result in unacceptably high (thermal explosion) or low (too long reaction time) rate of polymerization.

C.) Non-isothermal case

The condition (2.6) (constancy of κ) can be assured by the variation of the temperature according to a suitable program.

$$\kappa = \frac{\sqrt{W_1 k_4}}{k_2 m} = \sqrt{2f} \frac{\sqrt{k_1 k_4}}{k_2} \cdot \frac{\sqrt{x}}{m} = \text{const} \quad (2.15)$$

$\uparrow \quad \uparrow \quad \uparrow$
 const $T(t)$ t
 dependent

In this case, the variation of $x(t)$ and $m(t)$ is described by the following differential equations:

$$-\frac{dx}{dt} = k_1 [T(t)] x \quad (2.16)$$

and

$$-\frac{dm}{dt} = K [T(t)] \sqrt{x} \cdot m \quad (2.17)$$

Both are separable differential equations

$$-\int \frac{dx}{x} = \int k_1 [T(t)] dt \quad (2.18)$$

$$-\int \frac{dm}{m} = \int K [T(t)] \sqrt{x(t)} dt \quad (2.19)$$

For the integration of (2.18), the explicit knowledge of the function $T(t)$ is needed, when we obtain the following relationship:

$$x = x_0 \exp\{-\int k_1 [T(t)] dt\} \quad (2.20)$$

By the use of the latter, also (2.19) can be integrated (either analytically or numerically)

$$m = m_0 \exp\{-\int K [T(t)] \sqrt{x(t)} dt\} \quad (2.21)$$

It is rather obvious that the $T(t)$ function cannot be expressed explicitly. The problem reduces with the condition $T(t) = T_0 = \text{const}$ to the isothermal case treated in paragraph 2.B.

It is rather simple to control experimentally to what extent can the constancy of κ be assured in the case of a given temperature program. With consideration of the Arrhenius relationship, Equ. (2.15) can be given in the following form:

$$\kappa = \underbrace{\sqrt{2f} \frac{\sqrt{A_1 A_4}}{A_2}}_{\text{const.}} \underbrace{\frac{\sqrt{x(t)}}{m(t)}}_{f(t)} \exp\left\{-\frac{\Delta E}{RT(t)}\right\} \quad (2.22)$$

where

$$\Delta E = \frac{1}{2}(E_1 + E_4) - E_2 \quad (2.23)$$

The value of ΔE is, under usual conditions, 9-18 kcal/mol. Thus, the constancy/variation of $f(t)$ has to be controlled empirically with measuring of $x(t)$, $m(t)$ and $T(t)$. In the moment $t = 0$:

$$f(0) = \frac{\sqrt{x_0}}{m_0} \exp\left\{-\frac{\Delta E}{RT_0}\right\} \quad (2.24)$$

Consequently, a "quality factor" (Q) can be defined for the characterization of the experimental regime. Thus, Q can be given with the following expression:

$$Q = \frac{f(t)}{f(0)} \quad (2.25)$$

The nearer this quotient to 1, the better the experimental regime.

Based on the above outlined quantitative considerations, the following conclusions can be drawn.

Our method is based on the recognition that the above aim can completely be achieved if the desired degree of polymerization is maintained on a practically constant value by elevation the temperature according to a suitable program.

The method is based furthermore on the recognition that the regulation of the degree of polymerization by elevation the temperature can practically be realized by simulating the polymerization process using either an analytical formula or a numerical solution made by a computer and by conducting the real polymerization process according to the temperature program obtained from the simulation.

D.) The practical realization of the method

According to the practical realization of method, the degree of polymerization is regulated by the continuous elevation of the temperature according to a heat program determined by a function describing the variation of polymerization process against time with the aid of independent variables affecting the process, (the initiator concentration, monomer concentration, initial temperature, heating up time, desired degree of polymerization and polydispersity).

For the experimental realization of the heat program the Arrhenius equation(s) of decomposition rate constant(s) (k_1) of the initiator(s) as well as the Arrhenius equation of the quotient ($k_2/\sqrt{k_4}$) of the rate constants of

chain propagation (k_2) and of chain termination (k_4) characteristic of the monomer(s) must be known.

Under normal (isothermal) polymerization conditions, the polydispersity continuously increases during the process. Correspondingly, in our method the temperature must be elevated in such a way that the quotient $\kappa = k_{4r}/k_2m = \sqrt{(2k_1f_x \cdot k_4)}/k_2m$ remains constant at any time. Considering the Arrhenius relationships, this condition can be brought to the following form:

$$\kappa = \sqrt{2f} \frac{\sqrt{A_1 A_4}}{A_2} \frac{\sqrt{x(t)}}{m(t)} \exp\left(-\frac{\Delta E}{RT(t)}\right) \quad (2.26)$$

where $\Delta E = \frac{1}{2}(E_1 + E_4) - E_2$, and its value is 9 to 18 kcal/mole for various monomers, $m(t)$ is the momentary concentration of the monomer, $x(t)$ is the momentary concentration of the initiator, A_1 , A_2 and A_4 are the preexponential factors of the corresponding Arrhenius equations, $T(t)$ is the temperature program.

The "quality" of the temperature program applied to a given polymerization process, i.e. that of conducting the process can be controlled numerically as follows: at the moment $t = 0$, we obtain from Eq. (2.22):

$$f(0) = \frac{\sqrt{x(0)}}{m(0)} \exp\left(-\frac{\Delta E}{RT(0)}\right) \quad (2.27)$$

at every moment $t = t_i$ we calculate:

$$f(t_i) = \frac{\sqrt{x(t_i)}}{m(t_i)} \exp\left(-\frac{\Delta E}{RT(t_i)}\right) \quad (2.28)$$

The quality factor of the experimental regime can be composed from Eqs.(2.27) and (2.28):

$$Q_i = \frac{f(0)}{f(t_i)} \quad (2.29)$$

The closer is Q_i to unity, the better is the temperature program. In the practice some deviations always arise from the ideal temperature program, but the program is still sufficient if Q is an element of the following open interval:

$$0.95 < Q < 1.05 \quad (2.30)$$

The process according to the method makes possible to prepare α,ω -disubstituted copolymers of polydispersity optionally approaching the theoretical polydispersity and functionality from e.g. butadiene and other conjugated dienes, radically polymerizable vinyl monomers, such as acrylic and methacrylic esters, acrylo and methacrylo-nitrile, etc. Using the process, the main chain of the polymer formed from butadiene contains mainly monomer units incorporated in 1,4-position, i.e. the 1,4-cis + 1,4-trans-content is higher than 80 %.

The polymers prepared according to this method contain reactive end-groups in α,ω -positions, for example in the case of polybutadienediol (HTPBD) OH-groups, which enable the polymer to undergo further chemical reactions. Thus, for example, from polymer diols polyurethane can be produced.

The main advantages of the process according to our method are the following:

1. In case of a correct heat program, the conversion can be optionally increased without deterioration of the minimal polydispersity (\bar{P}_w/\bar{P}_n).

2. By suitable choice of the temperature program and of the initial concentrations, optional degree of polymerization can be obtained in the case of optimal initial composition.

3. It does not require surplus initiator as compared to that required in usual radical polymerization processes, and it makes possible the almost total using up of the initiator.

4. The practical execution of the temperature program does not require auxiliary equipment or use of surplus materials.

5. It can be carried out on a technological polymerization line already working. It can be easily automated, without major transformation of a technological equipment already in work.

3. § Experimental

Polymerization.

The experiments were carried out in an acid proof autoclave, Parr product. Nominal value of the autoclave is 1 litre, net volume 900 ml, maximum pressure allowed: 190 bar. The reactor is heated electrically from outside. The revolution number of the stirrer can be adjusted continuously, it has two propellers on the shaft. The reactor can be cooled by a spiral cooler with water circulation. The reactor has valves on the bottom and on the top.

The required amounts of solvent(s) and initiator(s) are filled into the open reactor, then it is closed and the stirrer started. After dissolution of initiator(s), highly purified nitrogen is pressed into the reactor through the bottom valve. After 5 minutes the nitrogen is blown off, than the autoclave

is evacuated to 10 mbar pressure. The above procedure with the nitrogen is repeated three times. After evacuation, the monomer previously filled into the buffer vessel and warmed to 30 °C is led into the reactor in liquid form. After the reaction mixture is filled in, the programmed heating of the reactor is started. During polymerization, the highest pressure is 15 bar in the system.

Materials used for the polymerization

1.) 4,4'-azo bis-4-cyano-n-pentanol (ACP): Synthesized in our laboratory from 5-hydroxy-2-pentanone (Fluka), Molecular weight: 252, Melting point: 81-83 °C or 94-96 °C (two isomers).

2.) Hydrogen peroxide: Peroxid Chemie GmbH product, Concentration: 50 % by weight.

3.) 1,3-Butadiene: Matheson product, Purity: 99.1 %.

The experimental conditions and the feed compositions of the polymerization are given in Table 1.

Table 1. Polymerization conditions and feed compositions.

Samples	Monomer (mol/l)	Solvent (ml)		Initiator (mol/l)		Polym.time (min)	Polym. 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-2	0.63	180	80-96
HTPBD-3000	6.0	400	-	2.14E-2	0.53	360	75-96
HTPBD-5000	6.0	400	-	5.73E-3	0.18	480	70-96
HTPBD-10000	6.0	200	200	8.0E-4	6.15E-3	720	70-96

Working-up of the polymerization mixture, purification of the polymer

After the polymerization is over, the reactor is blown off through the top valve. The unchanged monomer is condensed at -30 °C and recovered. After opening the reactor, the recombination product formed from the initiator and the main part of the unreacted H₂O₂ are removed from the polymerization mixture by washing with distilled water in a separatory funnel. The hydrogen peroxide remained after washing is decomposed by zeolite activated with cobalt ion, i.e. the washed reaction mixture is led through a column filled with zeolite and warmed to 40 °C by a heating jacket. The hydrogen peroxide content of the product is less than 1 ppm.

The solvents are removed from the reaction mixture in a film evaporator in nitrogen stream. The nitrogen is heated to 140 °C by regulated electric heating. The hot nitrogen goes to the evaporator tube, passing

through it at a rate 35-40 m/s. The solution to be evaporated is led to the inlet of the evaporator tube through a thin nozzle, and it is carried away by the fast nitrogen stream. The residence time of the product in the evaporator is 50-70 seconds. The pure polymer (i.e. freed from solvent and initiator residues) leaves the film evaporator at the gas separating valve.

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

The FT-IR spectra of the samples were recorded by a Bomem MB-100 spectrophotometer.

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 10^4 , 10^3 , 10^2 and 50 nm.

Determination of hydroxy groups content and functionality of the polymers

The functionality of the polymers can be calculated knowing the OH-endgroup concentration and the molecular weight of the polymers. The OH-content were determined by UV spectrophotometric method. First the OH-groups of the polymers were converted to carbamates in a reaction with a tenfold excess of phenyl isocyanate. The reaction was conducted in cyclohexane, in N_2 atmosphere, at room temperature for two hours. The unreacted phenyl isocyanate was removed with a twofold excess of n-propyl amine. The solution was diluted to $5 \cdot 10^{-5}$ - $12 \cdot 10^{-5}$ mol/l. The absorption

was measured at $\lambda = 236$ nm with a HP8452A UV spectrophotometer. The calibration curve was created using 1-hexadecanol as model compound (16, 17).

4. § Results and Discussion

We have synthesized six HTPBDs with nominal molecular weight from 1000 to 10000. Figure 1. and 2. show the computer created temperature program for the polymerization of HTPBD-1500 and HTPBD-10000, representing polymerization regime with ACP or ACP/H₂O₂ initiator, respectively. While in case of ACP the speed of heating is continuously increasing during the polymerization, with the mixed initiator system the initially increasing speed of heating slows down.

Table 2. shows the conversion of the polymerizations and GPC data of the polymers. The conversion varies from 10 to 40 %. Very low conversion was obtained for the HTPBD-10000 even with elevated butadiene concentration and extended reaction time. The explanation is the surprisingly low numerical value of k_2 (propagation) and the relatively high numerical value of k_4 (termination) of the butadiene, that is, its so called polymerizability value ($k_2/\sqrt{k_4}$) is low. In bulk and solution polymerization this value determines the rate and degree of polymerization.

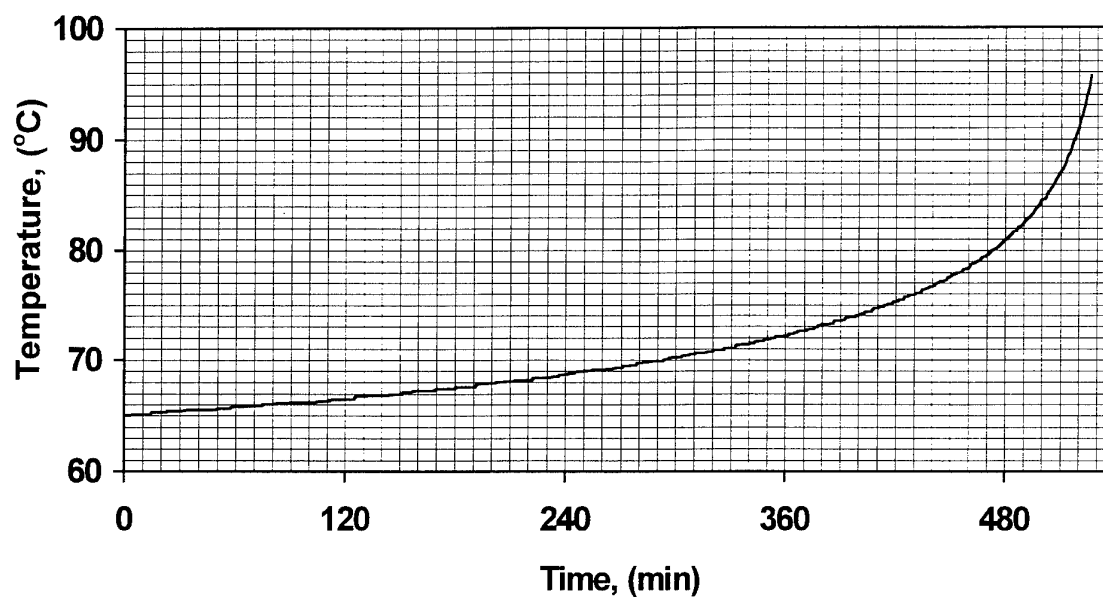


Figure 1. Temperature program for synthesis of HTPBD-1500.

Table 2. Conversion and GPC data of HTPBD samples.

Samples	Conversion %	GPC data	
		\bar{M}_n	\bar{M}_w/\bar{M}_n
HTPBD-1000	30	1245	1.34
HTPBD-1500	33	1552	1.34
HTPBD-2000	20	1870	1.62
HTPBD-3000	40	3250	1.98
HTPBD-5000	25	5230	1.72
HTPBD-10000	10	10800	1.95

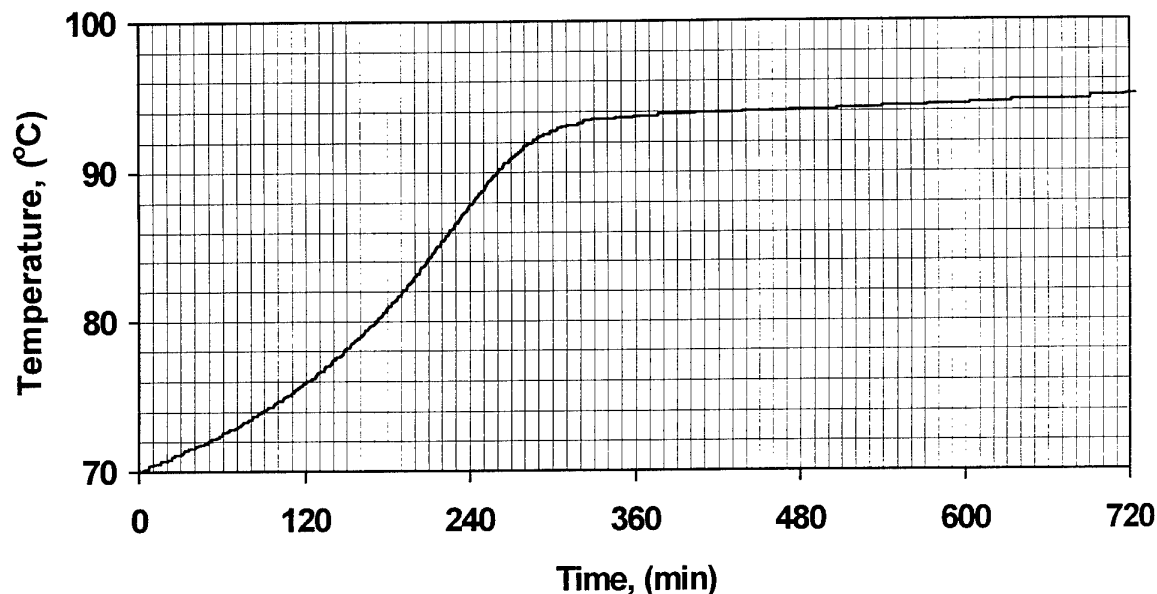


Figure 2. Temperature program for the synthesis of HTPBD-10000.

Figure 3. shows the molecular weight distribution of the six polymers. It is noteworthy that the molecular weight distribution of HTPBD-1000 and HTPBD-1500 is lower even than the theoretical value ($\bar{M}_w/\bar{M}_n = 1.5$). 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 ($\bar{M}_n < 1000$). Thus, the molecular weight distribution calculated by means of such calibration curve will be inaccurate to the same extent as the calibration curve itself.

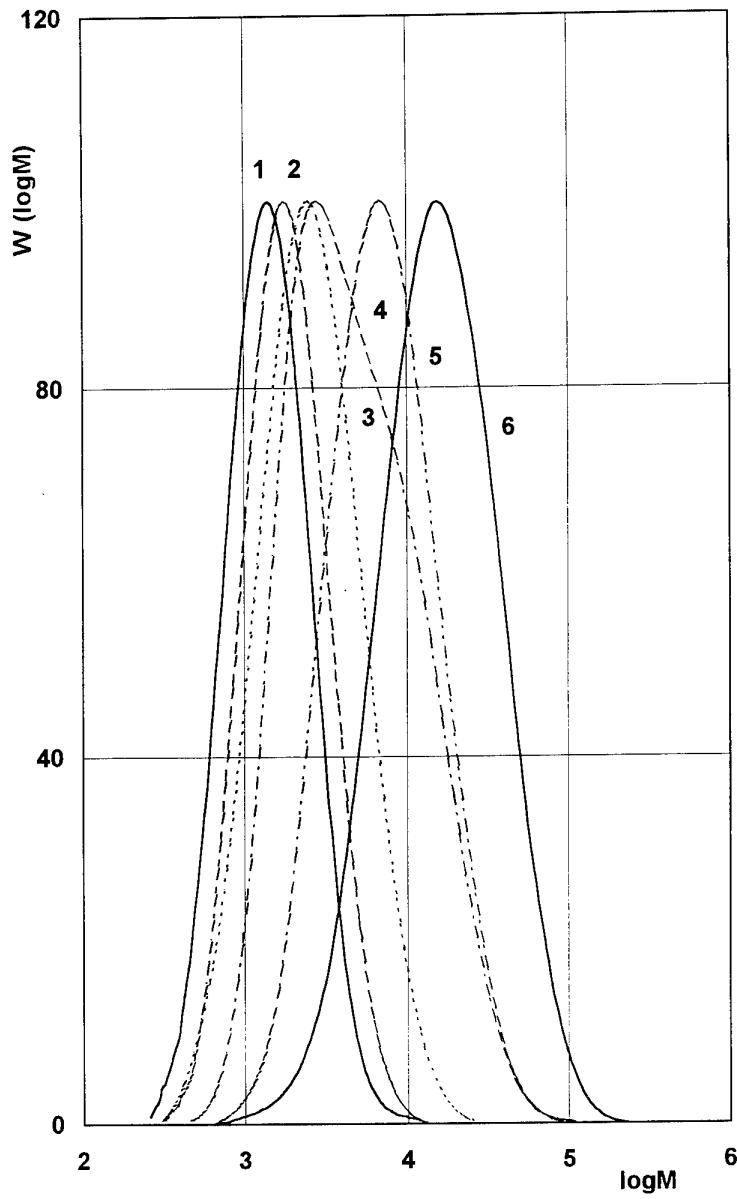


Figure 3. Molecular weight distribution of HTPBD samples.

1 = HTPBD-1000, 2 = HTPBD-1500, 3 = HTPBD-2000,
4 = HTPBD-3000, 5 = HTPBD-5000, 6 = HTPBD-10000

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_i stands for the growing active center and P for the polymer molecule formed) i.e. that is the numerical value of $k_{2,i}$ and $k_{4,ij}$ depends on the size of R_i and R_j (practically the degree of polymerization of the intermediate radicals).

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:

$$k_{2,i} = k_2 = \text{const.} \quad (4.3)$$

$$k_{4,ij} = k_4 = \text{const.} \quad (4.4)$$

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

$$1 \leq i, j \leq 20 \quad (4.5)$$

the above assumption is applicable only with restriction or not at all since the experimental results can 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. At this point we can conclude that the lower molecular weight distribution is even favourable for the preparation of the PU rubbers.

The microstructure of the samples were characterized by FT-IR and $^1\text{H-NMR}$. Figures 4. and 5. show the IR spectra of the six HTPBDs. The assignments of bands in the spectra are given in Table 3. The six 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 $3200\text{-}3600\text{ cm}^{-1}$ can not be seen. For the same reason the absorption of the $\text{-C}\equiv\text{N}$ group of the initiator fragments at $2218,7\text{ cm}^{-1}$ appears as a clear peak only in the spectra of the HTPBD-1000 and HTPBD-1500. In case of these polymers the intensity of the absorpition of the -OH and $\text{-C}\equiv\text{N}$ groups is also affected by the respective groups of the recombination product of the ACP initiator remained in the polymers.

Table 3. Bands in HTPBDs' spectra.

Band (cm^{-1})	Origin
3200 - 3500	OH stretch, associated form
3073.8	CH stretch of $\text{CH}_2=\text{CH}$
3004.3	CH stretch of cis- $\text{CH}=\text{CH}$
2915.6 - 2977.3	CH stretch of CH_2 , asymmetrical (ν_{as})
2844.2	CH stretch of CH_2 , symmetrical (ν_{s})
2218.7	CN stretch of $\text{C}\equiv\text{N}$
1636.9 - 1639.9	C=C stretch of $\text{CH}=\text{CH}$
1436.3 - 1447.9	CH_2 deformation (δ_{CH_2})
1405.4	CH in plane deformation of cis- $\text{CH}=\text{CH}$
1312.8 - 1350.4	OH deformation of prim. or sec. OH
1060.2	OH stretch of prim. or sec. OH
992.7	CH out of plane of $\text{CH}=\text{CH}$
965.7	CH out of plane of trans- $\text{CH}=\text{CH}$
911.7	CH_2 out of plane of $\text{CH}_2=\text{CH}$
720 - 740	CH out of plane of cis- $\text{CH}=\text{CH}$, and 1,2

Table 4. 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	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

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 965.7 cm^{-1} , 911.7 cm^{-1} and 722.7 cm^{-1} (see Table 4.). For the calculation we assumed that at the given wavelength only one structure has absorption. We used the molar extinction coefficients given in Table 5. and the equation below:

$$n_i = \frac{\frac{A_i}{\epsilon_i}}{\sum_1^i \frac{A_i}{\epsilon_i}} \quad (4.6)$$

where n_i , A_i and ϵ_i are the molar ratio, the absorption and the molar extinction coefficient, respectively. We have to emphasise that the weak absorption of the 1,4-cis units at $720\text{-}740\text{ cm}^{-1}$ can cause some uncertainty in the calculation.

Table 5. Molar extinction coefficient (ϵ) in polybutadienes (18).

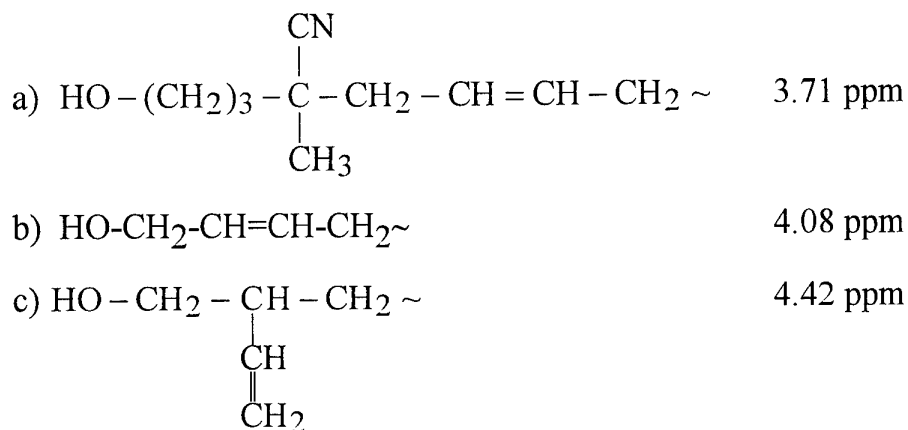
Component	Molar extinction coefficient, (ϵ)		
	965.7	911.7	722.7
trans-1,4	133	2.4	0.86
1,2	6.7	184	4.7
cis-1,4	4.4	1.9	10.1

The microstructure of the polymers determined by the FT-IR measurements were verified by the data based on the $^1\text{H-NMR}$ measurements. Figures 6-11. show the $^1\text{H-NMR}$ spectra of the samples. All six 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 $-\text{CH}=\text{C}-$ and $-\text{CH}=\text{CH}-$ groups formed from 1,2 and 1,4 linkages in the repeating units of polybutadiene appear at 4.9-5.0 and 5.2-5.4 ppm respectively. The ratio of integrals of the peaks belonging to the protons of these both groups gives the ratio of butadiene units built into 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 4.).

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 related structures at the chain-end:

Chemical shift:



Since HTPBD-1000 and HTPBD-1500 were synthesized using only ACP initiator the resonance at 4.08 ppm correlated to the protons in the HO-CH₂-CH=CH-CH₂-group (end group in case of H₂O₂-initiation) cannot be seen in the spectra of the polymers above.

The OH-functionality of the HTPBD samples were determined by UV spectrophotometric method. The measurement is not affected by the recombination product of the ACP initiator because it is not soluble in cyclohexane used as a solvent. The respective data are shown in Table 6.

Table 6. OH-functionality of the HTPBD samples.

Samples	Functionality
HTPBD-1000	1.62
HTPBD-1500	2.10
HTPBD-2000	1.90
HTPBD-3000	2.44
HTPBD-5000	1.98
HTPBD-10000	1.97

5. § Further theoretical problems

This Chapter gives theoretical account of some important points of isodisperse polymerization, emerged during the experimental work:

Determination of the limiting conversion

Calculation of initial temperature

Analysis of the function of the temperature program

A. Determination of the limiting conversion of isodisperse polymerization

Several aspects (first of all, the productivity of the process) require an end conversion of radical polymerization as high as possible (approaching or reaching 100 %). However, in the practice numerous theoretical and experimental difficulties are faced.

In the case of chemically initiated isothermal polymerization, Tobolsky (19) pointed out as early as in 1958 that for x_0 initial concentration of initiator, the maximum attainable conversion can be calculated by the following relationships (so-called "dead end" polymerization):

$$\log \frac{m_0}{m_\infty} = \frac{2}{k_1} K \sqrt{x_0} \quad (5.1)$$

where m_∞ is the concentration of remained (unpolymerized) monomer at $t = \infty$ time. The value of m_∞ can be expressed from (5.1):

$$m_\infty = m_0 \cdot \exp \left\{ -\frac{2}{k_1} K \sqrt{x_0} \right\} \quad (5.2)$$

Although the value of m_∞ is dependent on x_0 , it is plausible that m_∞ has a finite value at any value of the rate constants and of x_0 , i.e. it cannot be zero.

The limiting conversion of isodisperse polymerization can be calculated in an even simpler way. If x_0 initial concentration of initiator is used for the polymerization, then, assuming complete decomposition, it yields a total (integral) concentration of active centres

$$r_\Sigma = 2fx_0 \quad (5.3)$$

If the length of kinetic chain is ν_0 , and its value is kept constant by the technique of isodisperse polymerization, the amount of reacted monomer (Δm) is

$$\Delta m = m_0 - m_\infty = r_\Sigma \nu_0 \quad (5.4)$$

The value of v_0 is exactly fixed by the desired degree of polymerization:

$$\bar{P}_n = 2v_0 \quad (5.5)$$

On the other hand, the value of v_0 is unequivocally determined by the polymerization parameters:

$$v_0 = \frac{k_2 m_0}{\sqrt{2k_1 f x_0 \cdot k_4}} \quad (5.6)$$

The value of m_∞ from (5.4-6) is:

$$m_\infty = m_0 - r_\Sigma v_0 = m_0 - (2f x_0) \frac{k_2 m_0}{\sqrt{2k_1 f x_0 \cdot k_4}} \quad (5.7)$$

or

$$m_\infty = m_0 - r_\Sigma \bar{P}_n / 2 = m_0 - f x_0 \cdot \bar{P}_n \quad (5.8)$$

If the value of the limiting conversion is decided in advance, the required x_0 value can be chosen from (5.8):

$$x_0 = \frac{m_0 - m_\infty}{f \cdot \bar{P}_n} \quad (5.9)$$

Theoretically, the isodisperse polymerization allows even a 100 % conversion ($m_\infty = 0$). From this condition, the maximum possible x_0 can be calculated:

$$x_{0,\max} = \frac{m_0}{f \cdot \bar{P}_n} \quad (5.10)$$

B.) Calculation of initial temperature of isodisperse polymerization.

The initial temperature of isodisperse polymerization is determined by the value of \bar{P}_n , m_0 and x_0 calculated above. With the Arrhenius expression of the rate constants:

$$k_i = A_i e^{-E_i/RT} \quad (5.11)$$

\bar{P}_n can be brought to the following form:

$$\bar{P}_n = 2\nu_0 = 2 \frac{1}{\sqrt{2f}} \cdot \frac{A_2}{A_1 \cdot A_4} \cdot \frac{m_0}{\sqrt{x_0}} \exp\left(\frac{\Delta E}{RT_0}\right) \quad (5.12)$$

where

$$\Delta E = E_2 - \frac{1}{2}(E_1 + E_4) \quad (5.13)$$

T_0 can be expressed from (5.12):

$$T_0 = \frac{\Delta E}{R} \frac{1}{\log\left\{ \nu_0 \sqrt{2f} \sqrt{A_1 A_4 / A_2} \cdot \sqrt{x_0 / m_0} \right\}} \quad (5.14)$$

If the polymerization is started at T_0 temperature calculated this way, the polymerization degree of the polymer obtained will just correspond to the desired value. Further on, the change of m and x should be compensated by the temperature program.

C.) Analysis of the function of the temperature program

The kinetic condition of the isodisperse polymerization is the constancy of the following quantity (κ)

$$\kappa = \frac{k_4 r}{k_2 m} = \frac{\sqrt{W_1 k_4}}{k_2 m} = \text{const} \quad (5.15)$$

In the case of initiated polymerization $W_1 = 2k_1fx$, i.e.

$$\kappa = \frac{\sqrt{2k_1fk_4}}{k_2} \cdot \frac{\sqrt{x}}{m} \quad (5.16)$$

f(T) f(t)

The first term of the equation contains rate constants only, thus it is in the given case depending only on the temperature, the second term contains concentrations, and it is depending on the time. Under isothermal conditions, the first term remains constant, and the dependence of the second term on the time can be given by the following function:

$$f(t) = \frac{\sqrt{x_0} \cdot e^{-k_1 t/2}}{m_0 \exp\left\{-K\sqrt{x_0}\left(\frac{2}{k_1}\right)\left(1 - e^{-\frac{k_1}{2}t}\right)\right\}} \quad (5.17)$$

Let us introduce the following notations to this expression:

$$e^{-k_1 t/2} = y \quad (5.18)$$

and

$$K\sqrt{x_0}\left(\frac{2}{k_1}\right) = \gamma = 2k_2\sqrt{\frac{2f}{k_1k_4}}\sqrt{x_0} \quad (5.19)$$

Then

$$f(t) = \frac{\sqrt{x_0}}{m_0} \frac{y}{\exp\{-\gamma(1-y)\}} = \frac{\sqrt{x_0}}{m_0} y \exp\{\gamma(1-y)\} = \frac{\sqrt{x_0}}{m_0} f(y) \quad (5.20)$$

The limiting cases are:

If $y = 0$ ($t \rightarrow \infty$), then

$$f(t) = \frac{\sqrt{x_0}}{m_0} \cdot 0 \cdot \exp\{\gamma\} = 0 \quad (5.21)$$

If $y = 1$ ($t = 0$), then $f(1) = 1$, i.e.

$$f(t) = \frac{\sqrt{x_0}}{m_0} \cdot 1 = \frac{\sqrt{x_0}}{m_0} \quad (5.22)$$

Consequently, these two points are common points of all $f(y)$ functions, independently of γ . The plot of the $f(y)$ functions, at different γ values, is shown in the Figure 12.

Search of extremum:

$$\frac{d}{dy} \log \kappa' = 0 + \frac{1}{y} + 0 - \gamma = 0 \quad (5.23)$$

i.e.

$$\frac{1}{y_{\text{extr}}} = \gamma \quad (5.24)$$

or:

$$y_{\text{extr}} = \frac{1}{\gamma} \quad (5.25)$$

Since $0 \leq y \leq 1$, the above expression has physical meaning only if

$$\gamma > 1 \quad (5.26)$$

At the extremum:

$$\begin{aligned} f(t)_{\text{extr}} &= \frac{\sqrt{x_0}}{m_0} \frac{1}{\gamma} \exp\left\{\gamma\left(1 - \frac{1}{\gamma}\right)\right\} = \\ &= \frac{\sqrt{x_0}}{m_0} \frac{1}{\gamma} \exp(\gamma - 1) = \frac{\sqrt{x_0}}{m_0} \frac{1}{e\gamma} e^\gamma \end{aligned} \quad (5.27)$$

$f(\gamma)$

The Table of $f(\gamma)$

γ	$f(\gamma)$
0.01	37.16
0.5	1.21
0.9	1.0054
1	1
1.1	1.0047
1.5	1.099
2	1.359
3	2.463
4	5.021
5	10.92
10	810.3

Thus, there is always a maximum but, in terms of the present problem, it has physical meaning only in the case $\gamma > 1$.

If $\gamma \ll 1$, then in the interval $0 < y < 1$

$$f(y) \cong y, \text{ since} \quad (5.28)$$

$$e^{\gamma(1-y)} \approx 1$$

For sufficiently small γ values, $f(y)$ can be regarded as a linear function. Thus, if (i) $\gamma < 1$, the value of T should be increased in order to maintain κ at a constant value. If (ii) $\gamma > 1$, T should be first decreased, then, having passed the maximum of $f(y)$ it should be increased again and finally, if $f(y) \leq 1$, T should be increased to exceed T_0 .

Thus, the temperature program $[f(T)]$ is in the case (i) a convex (looking from above), exponential-like function, while in the case (ii) it is a minimum function. Of course, $f(T)$ can be determined only numerically. The program of its calculation was given in our 1st interim report.

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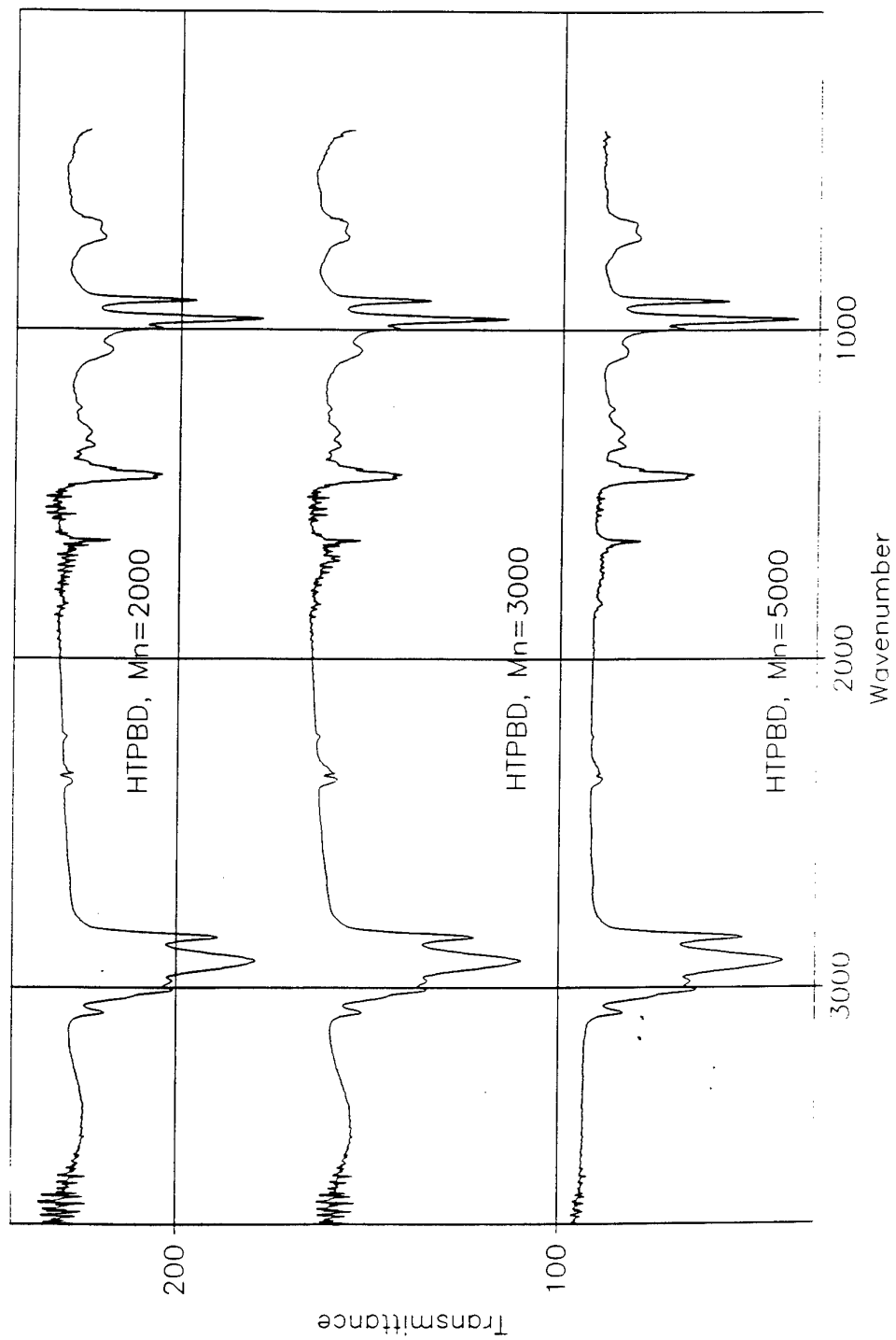


Figure 4. FT-IR spectra of polybutadiene diol samples.

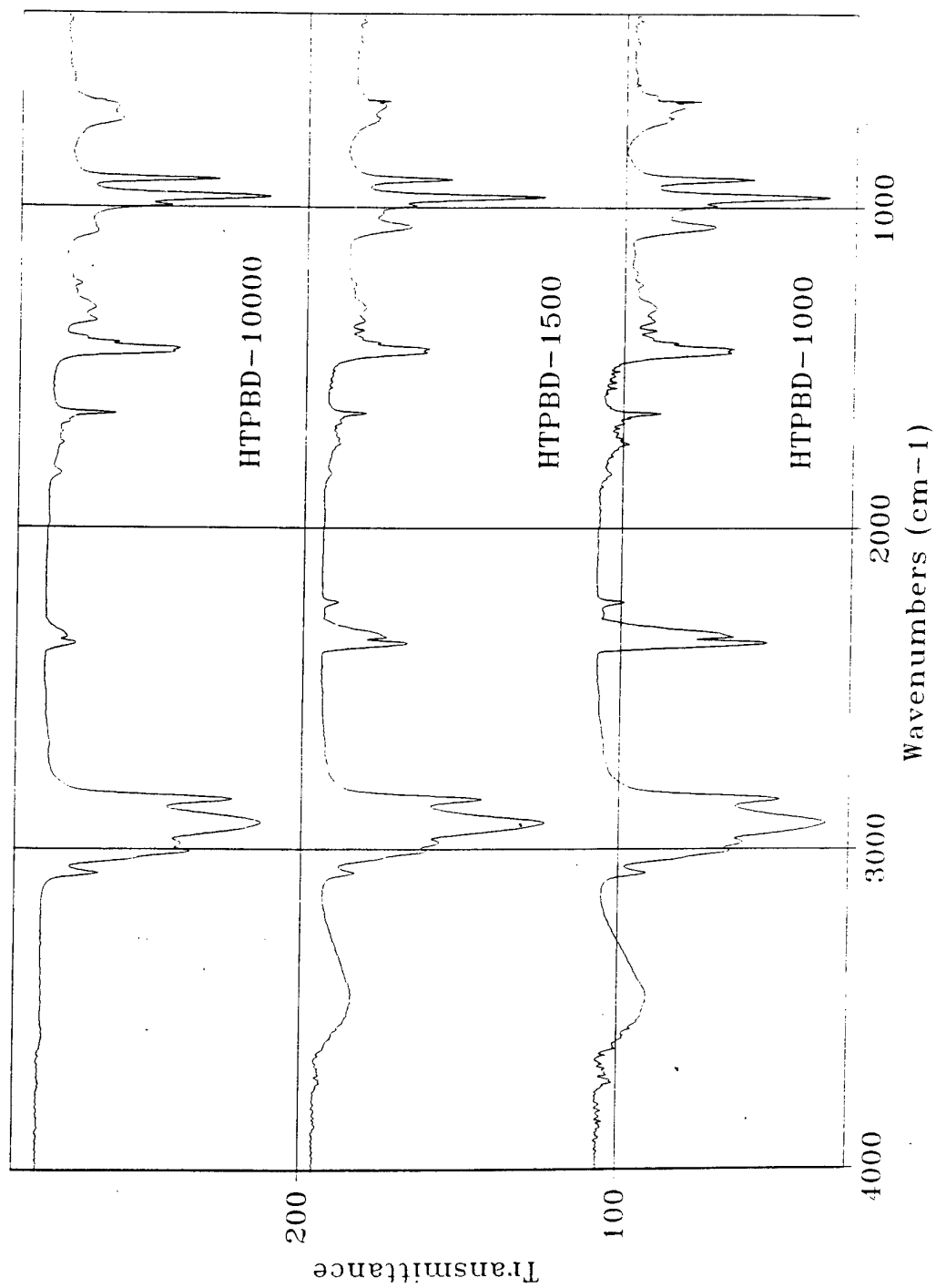
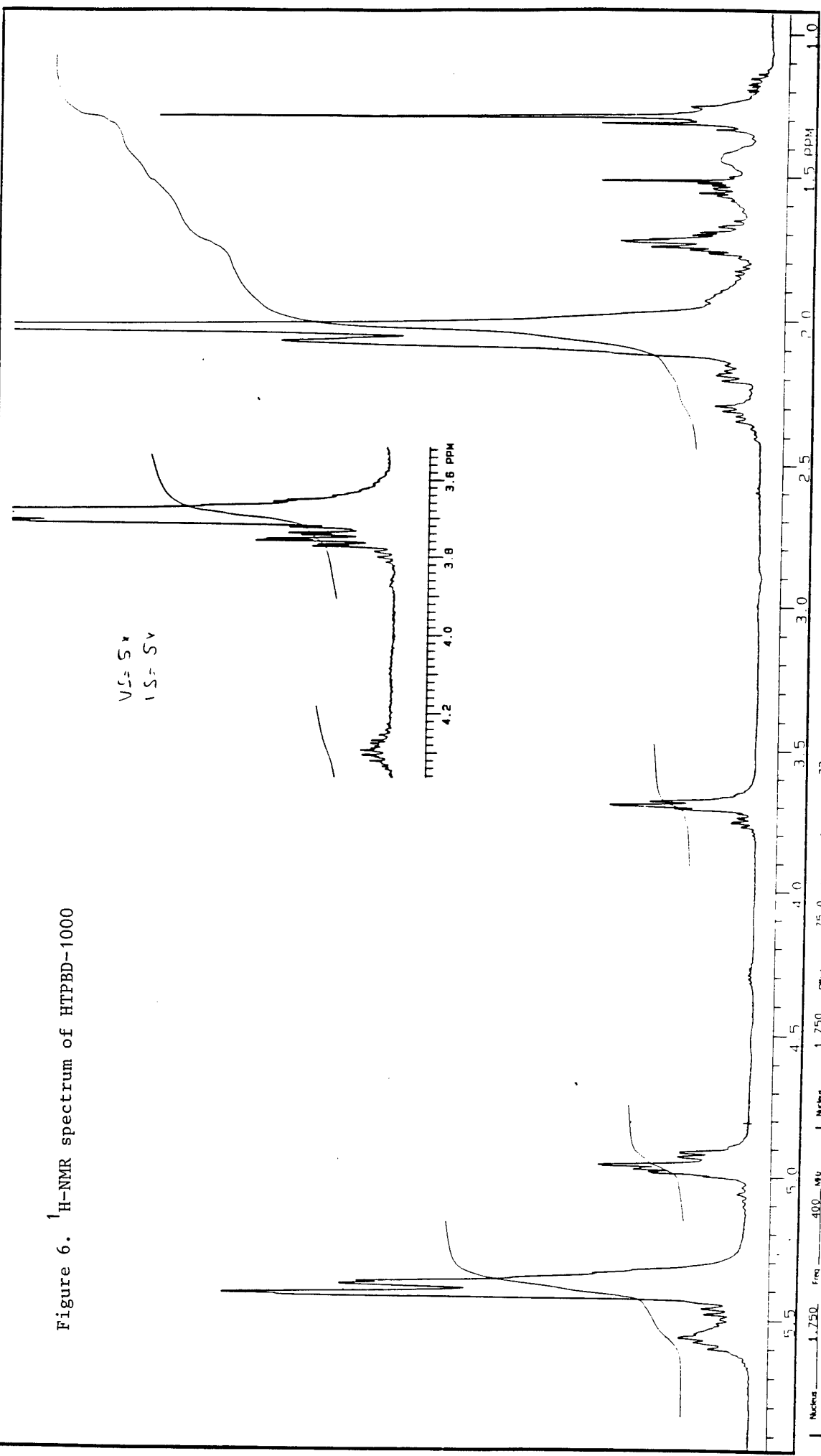


Figure 5. FT-IR spectra of polybutadiene diol samples.

Figure 6. ¹H-NMR spectrum of HTPBD-1000

V L = 5 *
I S = 5 v



Nucleus 1.750 Freq 400 MHz
 Spec Width 5800.5 Hz Offset 0 Hz
 Acq Time 3.994 sec Delay 0 sec
 Pulse Width 7.0 μ sec Transients 16

Nucleus 1.750 Offset 75.0 Hz
 Mode NNN Power 20 dB
 Modulation Mode C Freq 200 Hz
 Pulse Width 16 μ sec Power Mode ---

DECOUPLE
 P1 32 K P2 --- sec CD --- sec
 LB --- Hz AF --- sec CD ---
 Width 2006.1 Hz/ppm Start 372.1 Hz/ppm
 Reference ---

PLOT/PROCESSING
 Pulse Sequence STD1H
 Tube OD --- mm
 Temp --- $^{\circ}$ C
 Solvent CDCL3

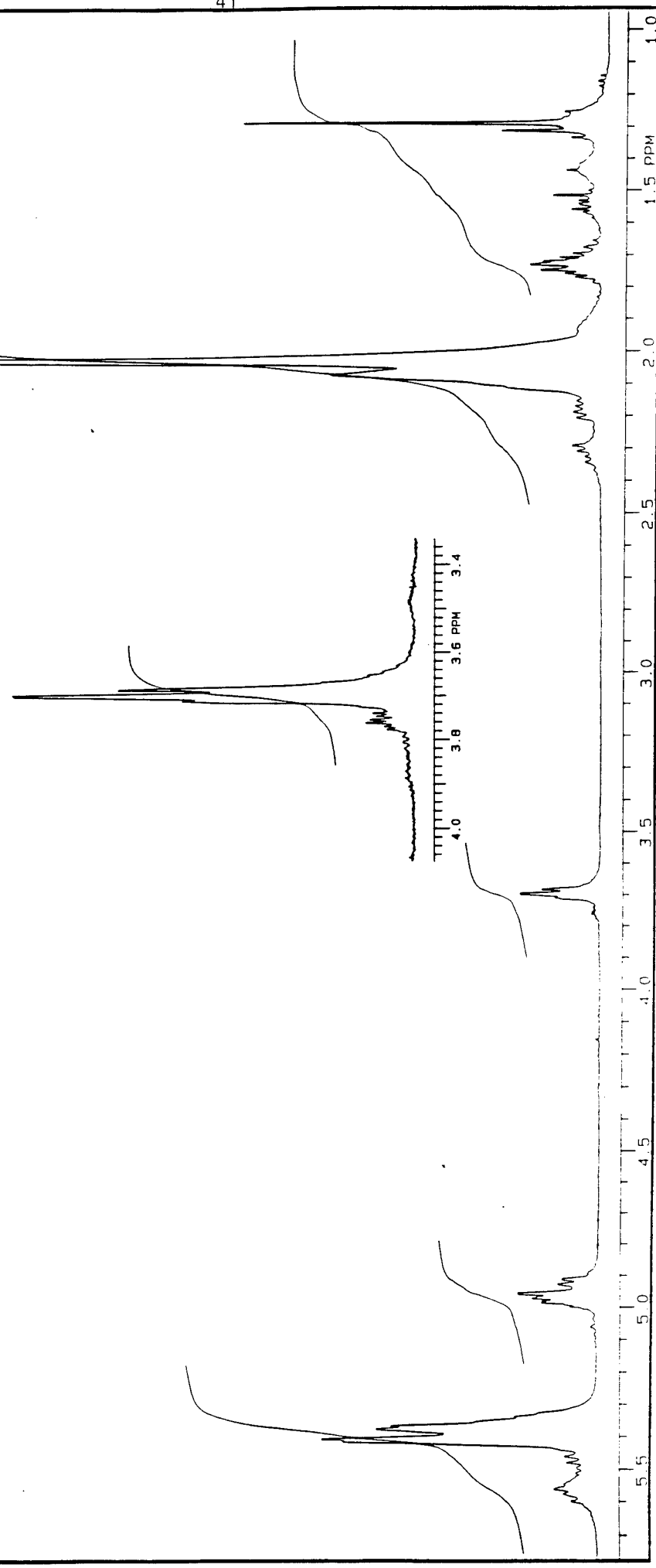
EXPERIMENT
 SAMPLE
 H-8218 (19414)
 130 (CDCL3)
 KESZLER B./E.O.

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

OBSERVE

Figure 7. ¹H-NMR spectrum of HTPBD-1500

US = 5 x
LS = 5 x



OPERATOR _____

REMARKS _____

Spec Width 5800.5 Hz **Off** _____ Hz **Mode** NNN **Power** 20 db

Acq Time 3.994 sec **Delay** _____ sec **Modulation Mode** C **Freq** 200 Hz

Scan Width 7.0 sec **Transmit** _____ sec **Pulse Width** _____ sec **Power Mode** _____

DECOUPLE _____

PLAT/PROCESSING _____

IN 32 K Hz **TE** _____ sec **CD** _____ sec

LB _____ Hz **AF** _____ sec **CCD** _____

Width 1933.1 Hz/ppm **Start** 376.7 Hz/ppm

Reference _____

EXPERIMENT

Pulse Sequence STD1H **SAMPLE**

Tube ID _____ mm **H-8219** (19414)

Temp _____ °C **137** (CDCL3)

Solvent CDCL3 **KESZLER B./E.O.**

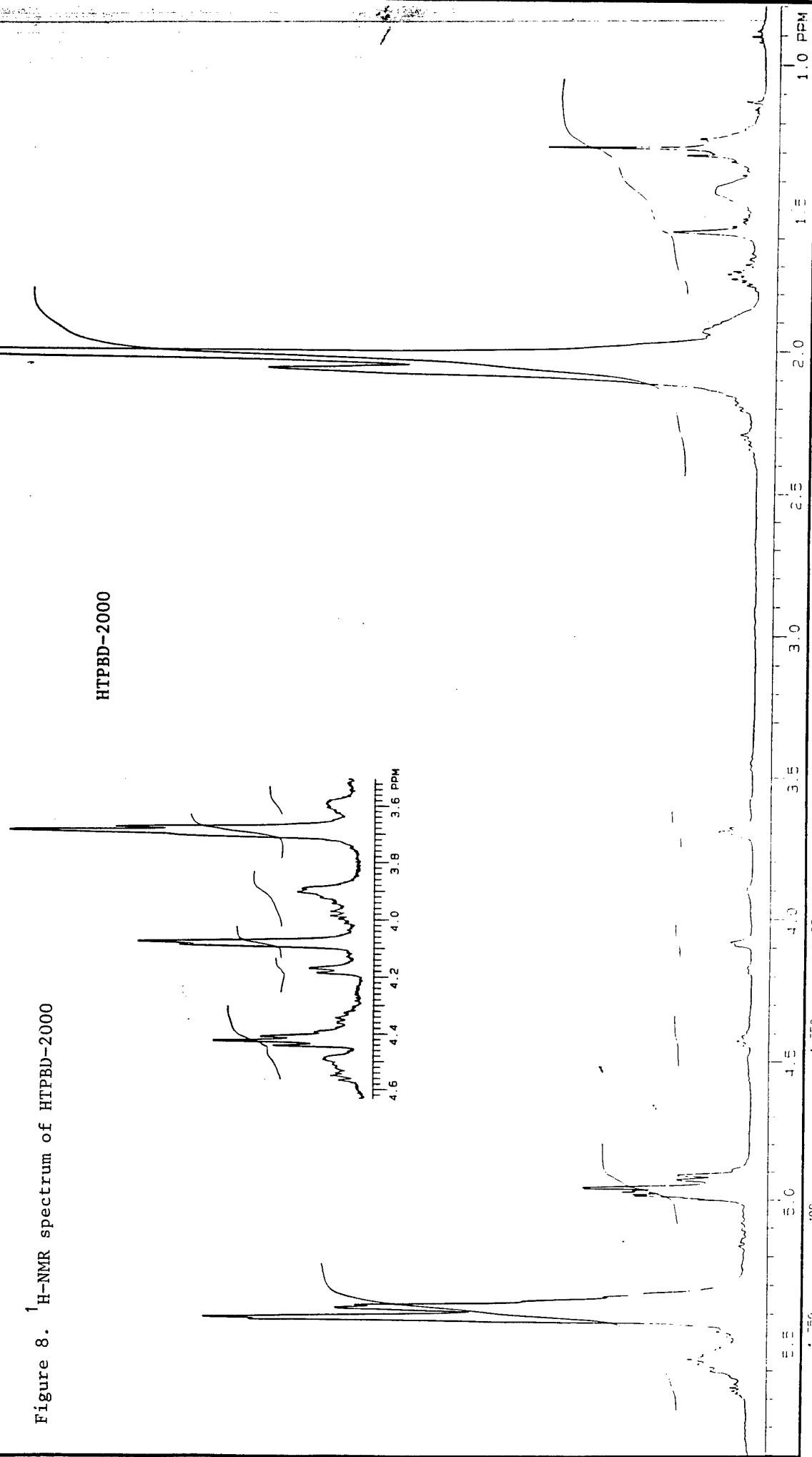
Number _____ **File** _____ **H**

Date 05-01-96 **VFA**

XL VXR 400MHz

Figure 8. ¹H-NMR spectrum of HTPBD-2000

HTPBD-2000



Nucleus: ¹H
 Spec Width: 5000 Hz
 Acq Time: 3.972 sec
 Pulse Width: 7.0 µsec
 Transmits: 16

Nucleus: ¹H
 Mode: MNN
 Modulation Mode: C
 Pulse Width: 16 µsec

Offset: 327.0 Hz
 Power: 20 db
 Freq: 200 MHz
 Power Mode:

FN: 327.0 Hz
 LB: 327.0 Hz
 WM: 20.40 Hz
 Reference:

Plot/Processing:

Experiment:

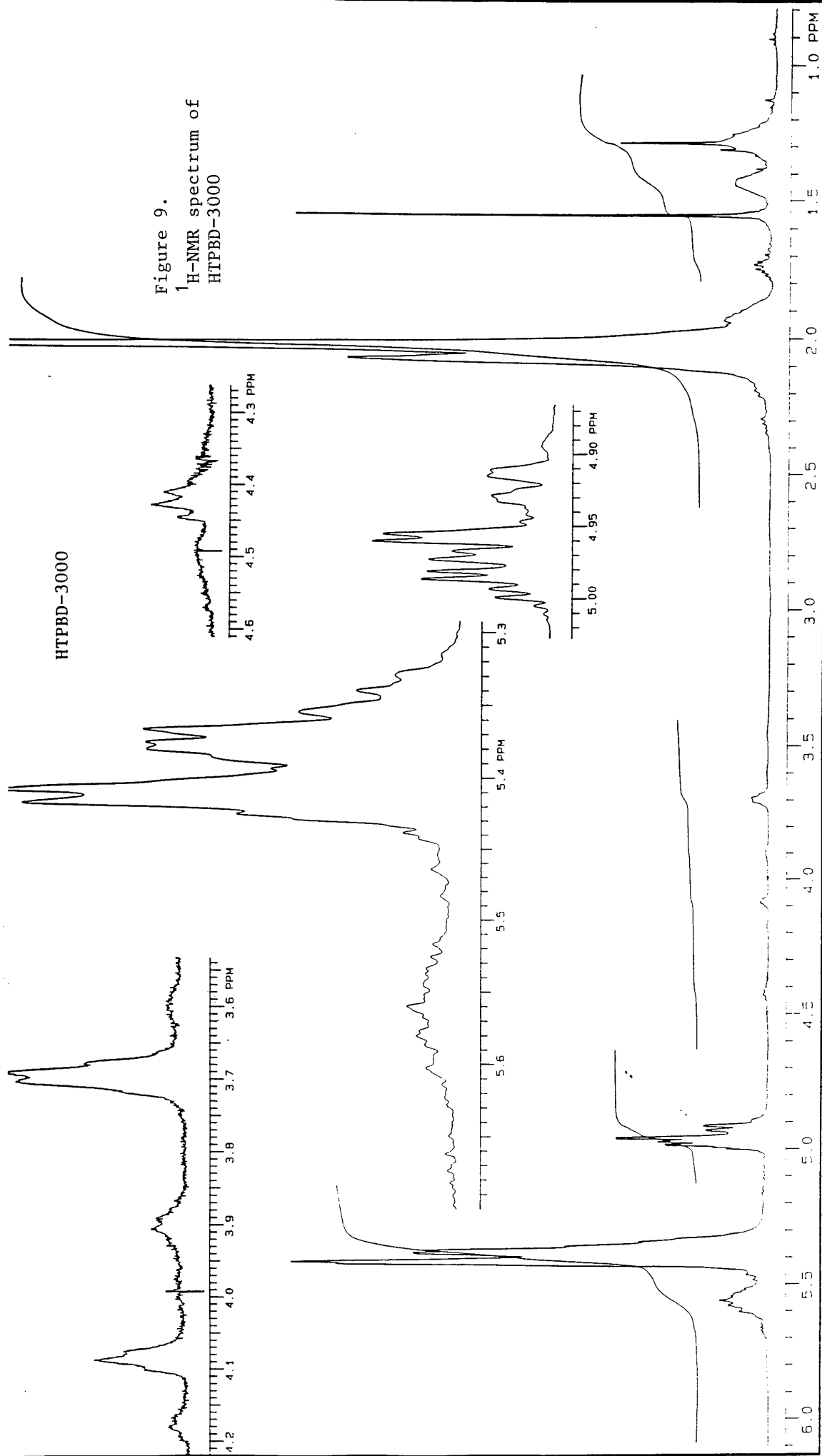
Pulse Sequence: STD:4
 Tube CD: mm
 Temp: °C
 Solvent: CDCL3

SAMPLE: H-737B (18600)
 POLIBUTADIEN (CDCL3) 70.4-1.4
 KESZLER B.V.E.O.

Number: HBE162
 File: 13-09-95
 Date: VXR 400 Varian XL

OSTRIVE

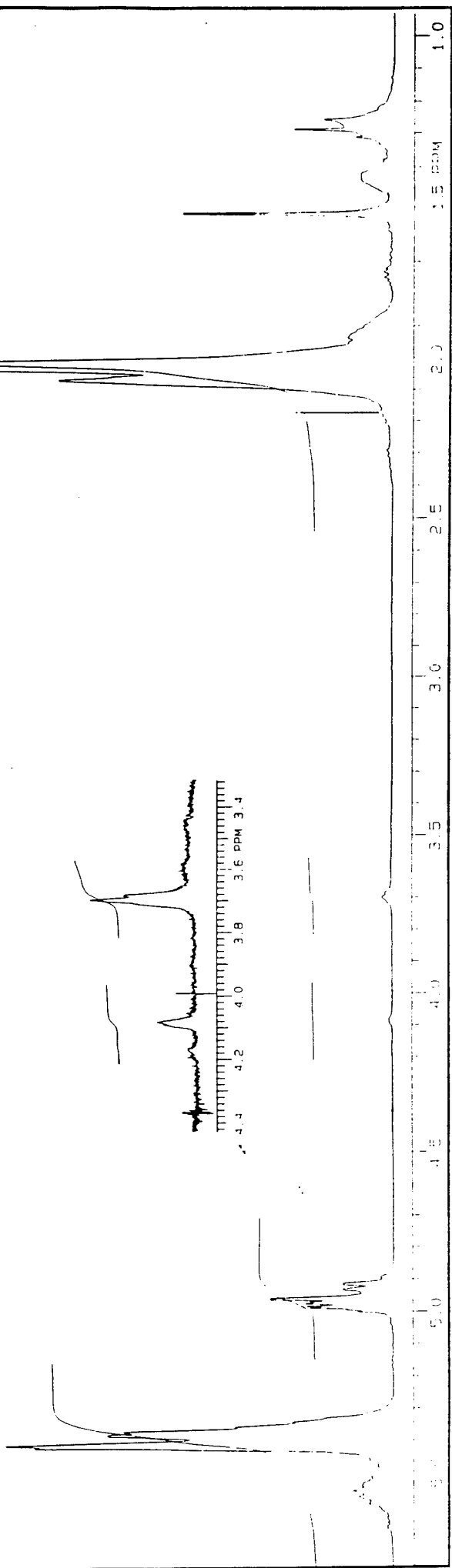
Figure 9.
¹H-NMR spectrum of
 HTPBD-3000



Observer	1 27 6	Freq	400 MHz
Solvent	CDCl ₃	Offset	-17.4 B
Acq Time	4.000 sec	Delay	0 sec
Proc Time	7.0 sec	Transmit	32
Magn	5.0	Mag	200
Modulation	Modulation	Power	200
Phase	Phase	Freq	300.1 Hz
Reference	Reference	Power	300.1 Hz
FM	32	WDW	Sum
GB	1.0	Sum	Sum
WDW	2139.0 Hz	Sum	Sum
Reference	Reference	Sum	Sum
Tube OD	mm	Temp	°C
Tube	mm	Solvent	CDCl ₃
Pure Source	CDCl ₃		
SAMPLE	4-7096 (18362)		
	116 (CDCl ₃)		
	KESZLER B./III.11.		
	PROTON SURVEY/G.E.		
INSTR	H		
FILE	21-06-95		
DATE	21-06-95		
XL	VXR		

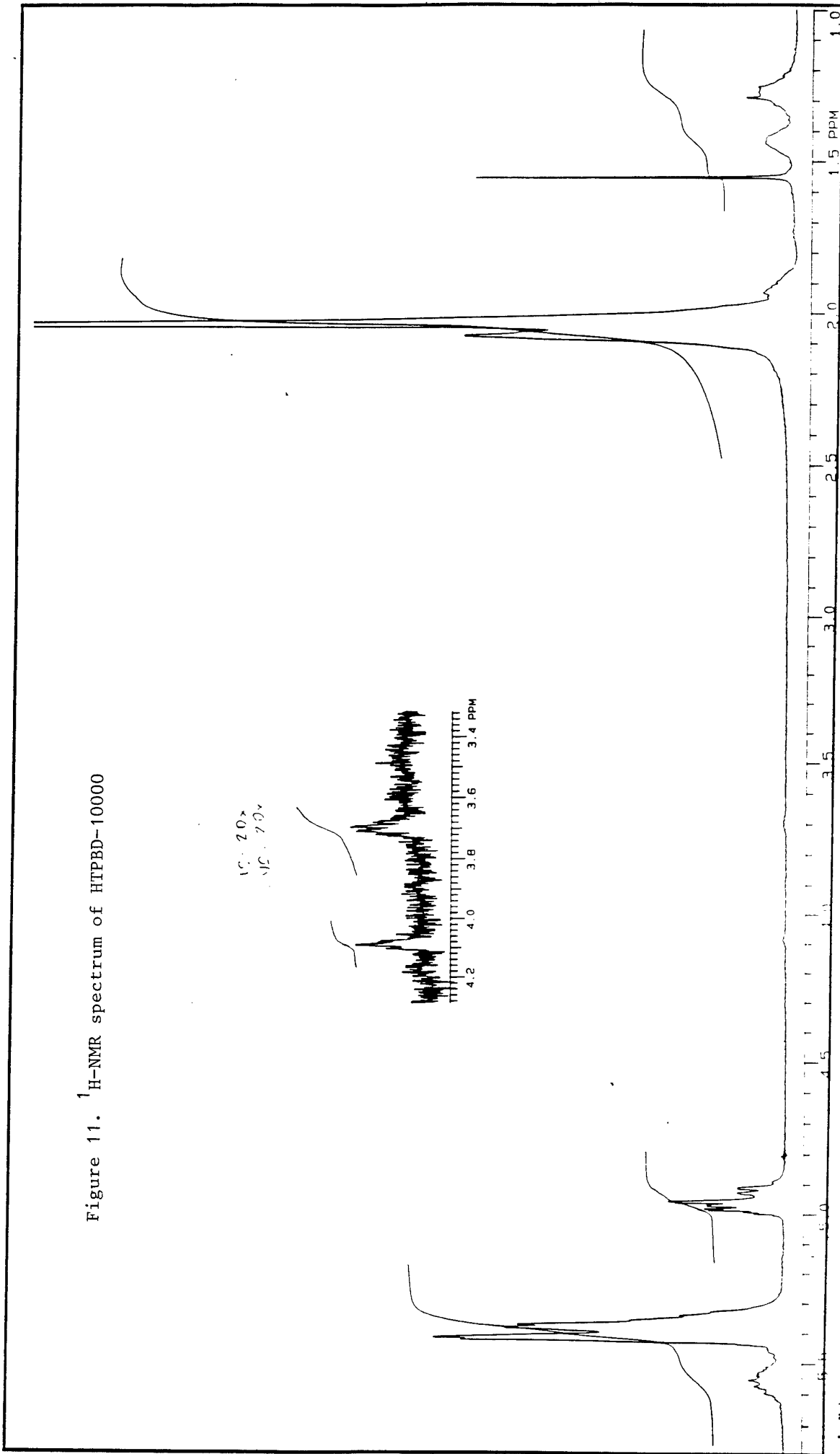
Figure 40. ¹H-NMR spectrum of HTPBD-5000

HTPBD -5000



OBSERVE		FREQ		400		MHz	
Pulse Width		10.0		0.0		µsec	
Acq Time		1.500		0		sec	
Modulation Mode		C		0		Hz	
Pulse Width		16		16		µsec	
Transmit		16		16		µsec	
RECEIVE		16		16		µsec	
Pulse Width		16		16		µsec	
Modulation Mode		C		0		Hz	
Power		20		20		dB	
Offset		20.0		20.0		Hz	
TURN		1.000		1.000		sec	
PLOT/PROCESSING		32		32		pts	
Reference		1947.1		372.3		Hz ppm	
Warm		1947.1		372.3		Hz ppm	
LB		---		---		Hz	
UB		---		---		Hz	
CD		---		---		Hz	
EXPERIMENT		---		---		Hz	
Solvent		CDCL3		CDCL3		---	
Temp		---		---		°C	
Tube OD		---		---		mm	
Pulse Source		S101H		S101H		---	
SAMPLE		H-7412 (18600)		K226H		---	
KESLER B.I.E.O.		PBH-126 (200.3)		K226H		---	
Date		14-09-95		K226H		---	
Run		XL		VXR		400 Varian	

Figure 11. ¹H-NMR spectrum of HTPBD-10000



Nucleus: ¹H Spec. Width: 4000 Hz Freq: 400 MHz Transm: 16 sec
 Spec. Width: 4000 Hz Acq. Time: 3.994 sec Delay: 0 sec
 Pulse Width: 7.0 μsec
 OBSERVE

Name: _____ Mode: UNN Modulation Mode: C Pulse Width: _____ μsec
 Mode: UNN Power: 20 dB Freq: 200 Hz Power Mode: _____
 Plot/Processing: _____ Width: 1917 g-Hz/gm Scan: 386 g-Hz/gpm Reference: _____
 LB: _____ Hz MC: _____ sec CD: _____ sec
 FN: 32.K RE: _____ MC: _____ CD: _____ sec

Pulse Sequence: STDH SAMPLE: H-8221 (19414)
 Tube OD: _____ mm HTPBD-10 (CDCL3)
 Temp: _____ °C KESZLER B./E.O.
 Solvent: CDCL3

Marker: _____ H: _____
 File: _____ Date: 05-01-96
 Operator: XI VXR 400VARIAN

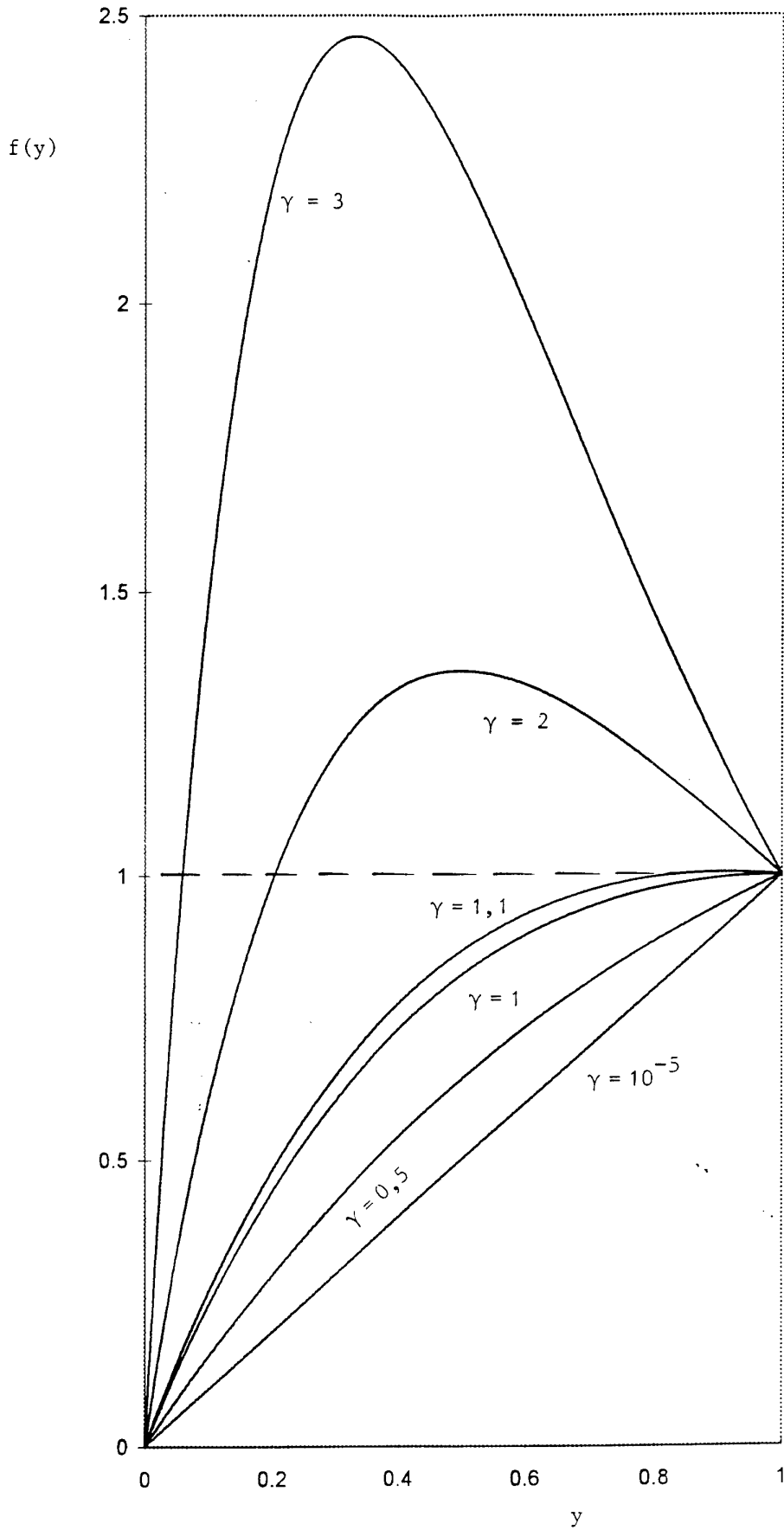


Figure 12.