Hydrogenation of Low-Molar-Mass, OH-Telechelic Polybutadienes. II. Nuclear Magnetic Resonance and Infrared Spectrometric Determination of Hydroxyl End Groups Before and After Hydrogenation by Diimide

J. PODEŠVA, J. SPĚVÁČEK, J. DYBAL

Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic,
Heyrovský Sq. 2, 162 00 Prague 6, Czech Republic

ABSTRACT: [1]H nuclear magnetic resonance (^{1}H-NMR), ^{13}C-NMR, and infrared spectroscopies were used to determine concentrations (c_{OH}, in mmol/g) of the secondary hydroxyl end groups in the low-molar-mass, OH-telechelic polybutadienes, and their hydrogenated analogs. Mean OH-functionality ($f_{OH} \leq 2$), that is, an average number of OH groups per one polymer chain, was calculated from c_{OH} for each sample and each method, and the results were compared with those obtained by a conventional acetic anhydride titration method. It has been found that with molar masses of the samples studied (2310 to 3410 g/mol), the differences between individual spectrometric methods are usually not higher than approximately 10%, which corresponds to an expected relative experimental error. Certain differences in f_{OH} between individual methods are discussed. No systematic change of f_{OH} after virtually total hydrogenation of the olefinic double bonds of the polymeric substrate by diimide was observed. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 3214–3224, 1999

Key words: telechelic polybutadienes; hydroxyl end groups; ^{1}H nuclear magnetic resonance spectroscopy; ^{13}C nuclear magnetic resonance spectroscopy; infrared spectroscopy

INTRODUCTION

Hydroxyl-telechelic polybutadienes represent a group of special advanced polymers, by processing of which various novel and valuable products can be obtained, applicable in many areas.[1] Most frequently, these commercially available polymeric diols are used as intermediates for the production of special types of elastomeric polyurethanes.

That type of hydroxyl-telechelic polybutadienes, which is studied in the present article, has a rela-

tively low molar mass (such materials are sometimes referred to as liquid rubbers) and is generally coded as PB throughout the text. It was prepared by a living anionic polymerization initiated by 1,4-dilithium-2-butene in methyl-*tert*-butyl ether. After the propagation had been completed, one molecule of propylene oxide was added to each of both living chain ends by a ring-opening mechanism. Finally, the end group C—O$^-$ Li$^+$ reacted with water, forming the OH group.[2] The resulting structure of both of the chain ends contains an exclusively secondary hydroxyl, $\sim\!\!\sim$(Bd)(Bd)CH$_2$CH(CH$_3$)OH, where Bd stands for a butadiene monomer unit irrespective of its isomeric structure.

Of course, spontaneous, undesirable termination of the living chains during the synthesis can never be fully avoided; consequently, some

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of the resulting polymer chains contain only one or even no OH end group, and the average OH functionality f_{OH} is, therefore, less than two. Since the application of these materials usually requires that this functionality is as close to two as possible, concentration of OH groups, c_{OH} (usually in mmol/g), is an important quantity, which should be determined with sufficient accuracy. A simple relation holds between these quantities, namely,

$$f_{OH} = 10^{-3} \times M_n \times c_{OH} \qquad (1)$$

where M_n is the number-average molar mass of the polymer. Although M_n is favorably low for PBs under study (in the order of magnitude of thousands), measuring c_{OH} still represents a typical analytical problem of determination of small concentrations. Usually, in practice, c_{OH} is measured by a proper titration method, based on the reaction of OH groups with, for example, acetic anhydride.[3]

Although PBs are very useful materials, they exhibit, as a consequence of the reaction between their olefinic double bonds and air oxygen, rather low thermooxidation stability, which can only partially be improved by antioxidants. Obviously, saturation (hydrogenation) of C=C bonds of PB's would prevent such undesirable oxidation completely, but the respective polymer analogous reaction must be chosen so that resulting hydrogenated analogs (HPBs) have essentially unchanged concentration of the OH end groups. A corresponding two-step hydrogenation procedure, consisting of prehydrogenation by gaseous hydrogen (catalyzed by Ziegler–Natta systems) in the first step and diimide hydrogenation of the residual C=C bonds in the second step, is described in a separate article.[4]

It has therefore been our aim to find out if and precisely how the values of c_{OH} can be determined by various spectrometric methods [^{13}C nuclear magnetic resonance (NMR) and ^{1}H-NMR, and infrared (IR) spectroscopy] in this case, both before and after hydrogenation. We have also tried to decide whether or not the quantity c_{OH} changed during this reaction. Determination of other characteristics, like concentration of residual olefinic double bonds, free contaminants, and/or substituents is discussed elsewhere.[4]

EXPERIMENTAL

Materials

Unsaturated Polymers

Three samples of the low-molar-mass, hydroxyl-telechelic polybutadiene (PB) were used. They were commercial products by Kaučuk Group AS (Kralupy n. Vlt., Czech Republic), purchased under the trademark Krasol LBH, batches No. 3000-27/93 (sample PB-1), 005 (sample PB-2), and 3000-C017 (sample PB-3). The following parameters were given by the manufacturer: number-average molar masses, 2310, 3290, and 2600 g/mol; mass-to-number average molar mass ratios, 1.13, 1.14, and 1.23, respectively; concentration of the OH groups in the bulk polymer, 0.765, 0.589, and 0.757 mmol/g, which corresponds to an average OH functionality of 1.77, 1.94, and 1.97, respectively; and stabilization of all samples, Irganox 1520 D, that is, 2-methyl-4,6-*bis*[(octylthio)-methyl]phenol, 0.2%. Content of isomeric structures for all samples was as follows: 60% 1,2, 15% 1,4-cis, and 25% 1,4-trans (in comparison, we have determined the fraction of the 1,2 structure by ^{1}H-NMR to be 63.6, 62.0, and 63.1%, respectively).

Saturated Polymers

All samples of saturated polymers (HPB), coded as H-1 through H-9, were prepared by hydrogenation of either PB-1 or PB-2. These starting substrates were hydrogenated either directly (in one step) by diimide, a substance generated by a thermal decomposition of *p*-toluenesulfonylhydrazide, or in two steps, via a partially saturated intermediate, prepared by prehydrogenation up to some 95% using gaseous hydrogen and a Ziegler–Natta catalytic system, and then finished by diimide up to virtually 100% (for details, see Podešva and Holler).[4]

NMR Measurements

^{13}C- and ^{1}H-NMR spectra were recorded with a Bruker DPX-300 spectrometer at 75.5 and 300.1 MHz, respectively. 20% (*w/v*) solutions in CDCl$_3$ were measured at room temperature in 5-mm NMR tubes. Hexamethyldisiloxane, with a signal at 2.0 ppm from TMS in ^{13}C spectra and at 0.05 ppm in ^{1}H spectra, was used as an internal standard; chemical shifts in the text and figures are referred to TMS. In conventional ^{13}C-NMR spec-

tra, 90° pulses were used with 4000–5200 scans, 26,455-Hz spectral width, and 0.62-s acquisition time. For reliable quantitative analysis, sample PB-1 was measured with the following three different values of relaxation delay: 6, 10, and 15 s. Since no difference was found for quantities determined with relaxation delays of 10 and 15 s, all other samples were measured with relaxation delay of 10 s. In addition to conventional ^{13}C-NMR spectra, attached proton test[5] (APT) spectra were also measured in some cases; these spectra enabled us to determine whether the number of hydrogens attached to a carbon also bearing the hydroxyl group is odd (one in our case) or even (zero or two). In measurements of ^{1}H-NMR spectra, we used 90° pulses with 32 scans, a spectral width of 5995 Hz, an acquisition time of 2.73 s, and a relaxation delay of 6 s.

IR and Raman Measurements

IR and Raman spectra were recorded with a Fourier transform infrared (FTIR) spectrometer Bruker IFS-55, equipped with a Raman modul FRA-106 (Nd: YAG laser, 1064 nm). Spectra were measured with a resolution of 2 cm^{-1}. For treating the spectra (subtracting the spectra of solvents and separation and integration of the peaks), a commercial software OPUS was applied. For measurements of bulk, solvent-free samples, thin layers between KBr windows were used, whereas the solutions were measured in KBr cells having thicknesses of 0.98 and 0.602 mm.

Determination of Hydroxyl End Groups by a Titration

A procedure, described by, for example, Siggia,[3] was modified as follows. The acetylation mixture was prepared by a dissolution of 2.4 g of p-toluenesulfonic acid in 60 mL of ethyl acetate, followed by an addition of 8.5 mL of acetic anhydride. In a standard analytical run, 5 mL of the acetylation mixture was mixed with 2 g of the sample. The mixture was kept at 50°C for 30 min, then 2 mL of water was added. After vigorous shaking, 5 mL of pyridine–water (1/1 v/v) mixture was introduced, and the mixture was left standing for 5 min. The precipitated polymer was redissolved by an addition of 25 mL of chloroform, and the resulting mixture was titrated by 0.2M KOH in methanol, using phenolphthalein as an indicator. Under identical conditions, a blank determination was also performed without the sample. The quantity c_{OH} (mmol/g) was then calculated according to the following equation:

$$c_{OH} = (V_b - V)fc_M/m \qquad (2)$$

where V_b and V are volumes (in mL) of the titration solution consumed for the blank experiment and for the sample, respectively. Symbols f, c_M, and m denote, respectively, the factor of the titration solution, the mole concentration (in mol/L) of the titration agent, and the mass (in g) of the sample.

RESULTS AND DISCUSSION

NMR Spectra

^{13}C- and ^{1}H-NMR spectra of the original, unsaturated Krasol LBH polymers (PB) are illustrated in Figure 1 by the example of the sample PB-1. The resonances of olefin carbons are in the left part, while those of aliphatic ones are in the right part of the ^{13}C spectrum in Figure 1(a), where the assignment to various carbons of 1,4- and 1,2-PB units is also given. The most interesting resonances are the three peaks in the range 65.5–67.7 ppm, where the resonances of carbons bound to hydroxyl end groups are reported to occur.[6,7] APT spectrum of the sample PB-1 confirmed that all the three resonances correspond to CH carbons, evidently from the —CH(CH$_3$)—OH end groups. Existence of these three resonances is very likely the consequence of a nonuniform microstructure (1,2-, 1,4-trans, and 1,4-cis) of the ultimate PB monomer unit (it should be kept in mind that the very end of the chain was formed by adding a molecule of propylene oxide). The analysis of the olefinic region in ^{1}H-NMR spectra [4.8–5.8 ppm; Fig. 1(b)] suggests that sample PB-1 contains 63.6% 1,2-units (for the microstructure of PB-2 and PB-3, see the experimental, materials section). Hence, the strongest line at 65.6 ppm in Figure 1(a) probably corresponds to the —CH(OH)— carbon following the 1,2 monomer unit. In the ^{1}H-NMR spectrum [Fig. 1(b)], the multiplet at 3.79 ppm can be assigned[8,9] to methine protons of the —CH(CH$_3$)OH end groups.

From integrated intensities of hydroxylated carbons (I_{OH}) in the range 65.5–67.7 ppm in ^{13}C spectra or the band at 3.79 ppm in ^{1}H spectra and integrated intensities of lines of all PB carbons or protons (I_{PB}), the mole ratio m of hydroxyl groups
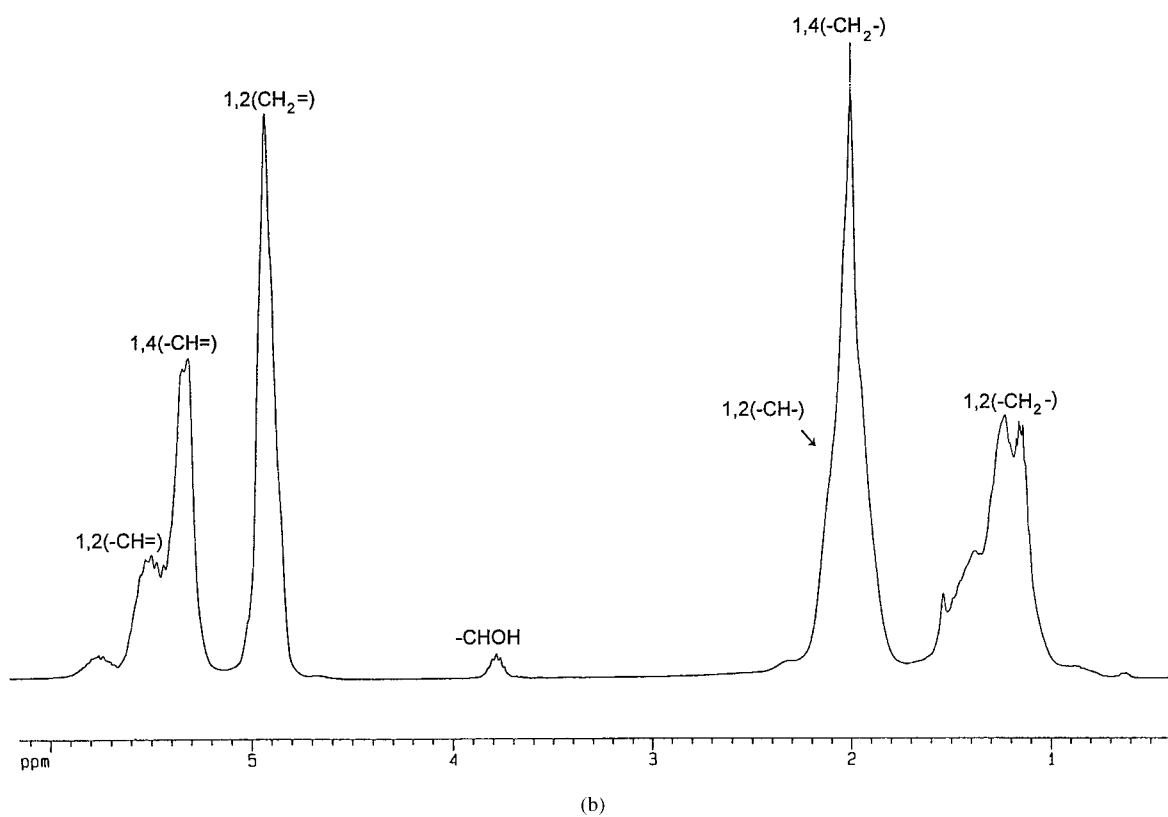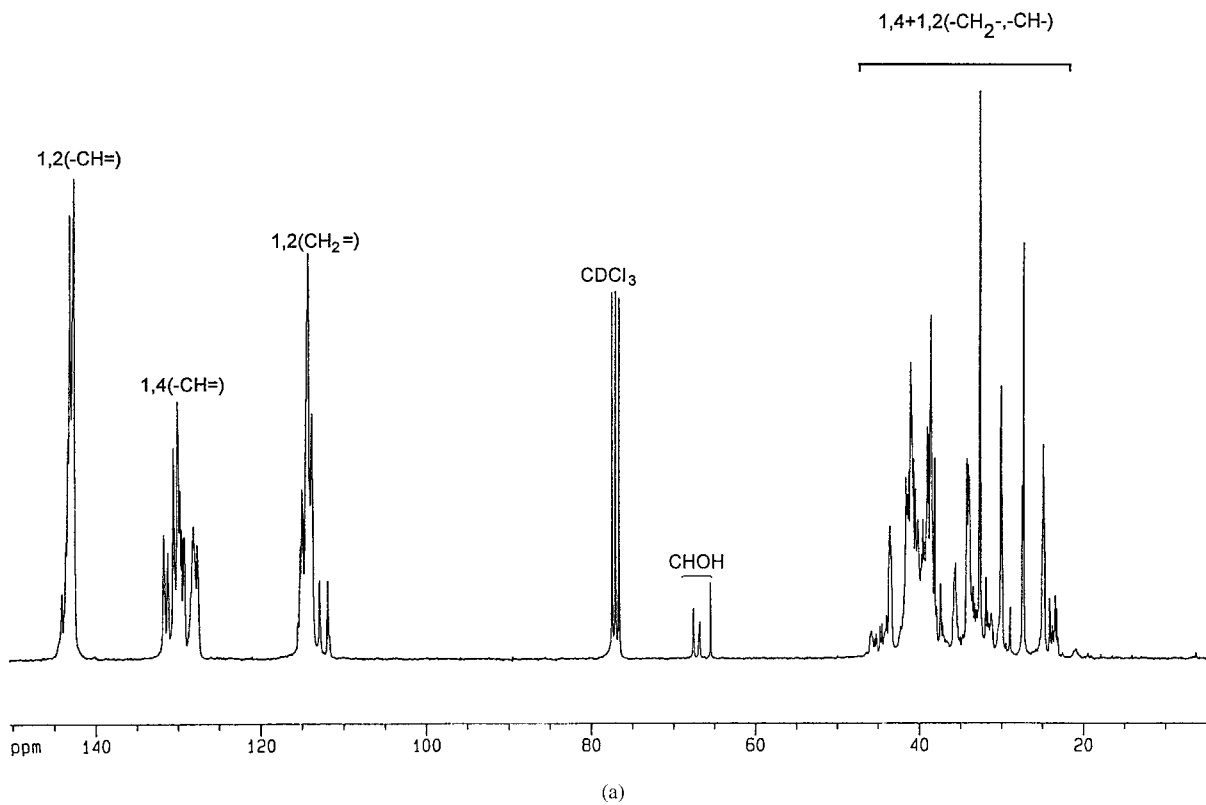
Figure 1 (a) 75.5-MHz ^{13}C-NMR spectrum and (b) 300.1-MHz ^{1}H-NMR spectrum of the sample PB-1 in CDCl$_3$ at ambient temperature.

Table I Concentration of OH Groups c_{OH} (mmol/g) in Samples of Polybutadienes Krasol LBH (PB-1 to -3) and their Hydrogenated Derivatives (H-), as Determined by Spectroscopic and Titration Methods

Sample Code	^{13}C-NMR	^{1}H-NMR	IR	Titration
PB-1	0.64	0.64	0.80	0.76_5
H-1[a]	—	0.58	0.69	—
H-2[a]	0.76	0.64	0.76	0.66
PB-2	0.65	0.53	0.75	0.59
H-3[b]	0.65	0.52	0.68	—
H-4[b]	—	0.48	0.56	—
H-5[b]	0.60	0.58	0.56	—
H-6[b]	0.55	0.50	0.58	—
H-7[b]	—	0.60	0.58	—
H-8[a]	—	0.46	0.56	—
H-9[a]	—	0.45	0.50	0.45
PB-3	0.61	0.66	0.72	0.76

H-1 and H-2 were prepared by hydrogenation of PB-1; other samples were prepared by hydrogenation of PB-2.

Products of hydrogenation were purified in the final step by [a]column chromatography or [b]reduction cleavage (see Podešva and Holler[4]).

and PB monomer units was determined, as follows:

$$^{13}\text{C-NMR:} \quad m = I_{OH}/(I_{PB}/4) \quad (3a)$$

$$^1\text{H NMR:} \quad m = I_{OH}/(I_{PB}/6) \quad (3b)$$

The quantity m can be transformed into the concentration of hydroxyl groups, c_{OH} (in mmol/g), according to the following relation:

$$c_{OH} = 10^3 \times (m/M_B) \quad (4)$$

where M_B is molar mass (in g/mol) of PB monomer unit (54.09 g/mol). The values obtained are shown in Table I.

In Figure 2, the ^{13}C- and ^{1}H-NMR spectra of almost completely hydrogenated Krasol LBH samples (HPB) are illustrated by a typical example (sample H-2). In the ^{13}C-spectrum [Fig. 2(a)], the resonances around 11 ppm correspond to CH_3 carbons of hydrogenated 1,2-units, while CH and CH_2 carbons resonate in the range of 24–46 ppm. Only two lines of the —CH(OH)— carbons of the end groups are seen at 66–68 ppm. Weak resonances exist around 130 ppm. These lines could correspond only partly to residual olefinic me-

thine carbons from 1,4-units because a very small amount of olefinic protons was found in ^{1}H-NMR spectra [at 5.3 ppm, Fig. 2(b)]. Since ^{1}H spectra reveal that hydrogenated samples contain a certain amount of structures bearing aromatic protons, the ^{13}C resonances in the range of 125–142 ppm most probably originate prevailingly from aromatic carbons of these structures. Two bands at 3.68 and 3.79 ppm in ^{1}H spectra were assigned to the methine CH(OH) protons.

The quantitative analysis of hydroxyl groups in HPBs is similar to that described for PBs, provided the effect of aromatic structures can be neglected, as follows:

$$^{13}\text{C-NMR:} \quad m = I_{OH}/(I_{HPB}/4) \quad (5a)$$

$$^1\text{H-NMR:} \quad m = I_{OH}/(I_{HPB}/8) \quad (5b)$$

where I_{HPB} are integrated intensities of lines of all HPB carbons or protons. A relation similar to eq. (4) holds here, except that the molar mass of the hydrogenated monomer unit, $M_{HB} = 56.11$ g/mol, is used instead of M_B. Again, the results are gathered in Table I. Discussion on the data is given below, together with that of IR measurements.
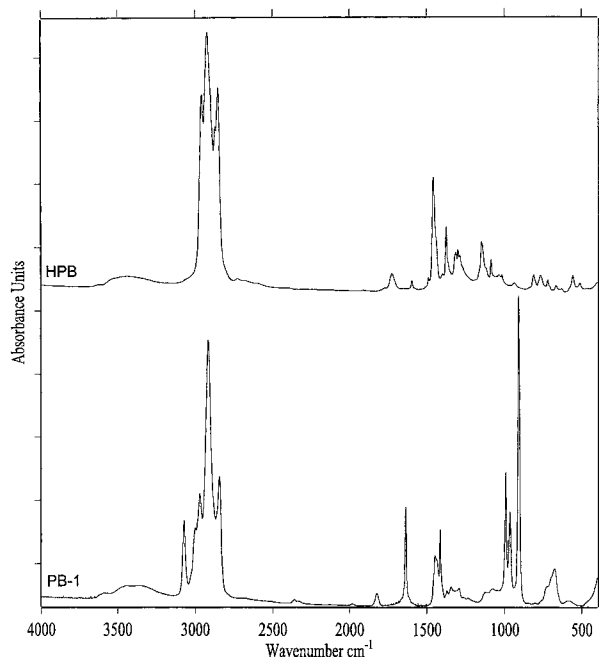
IR and Raman Spectra

Two solvents were used for the solution measurements of the IR spectra, namely, heptane (HEP) and tetrahydrofuran (THF). All the spectra of polymers, measured in the form of solutions and given in figures, are presented after subtraction of the corresponding spectra of the solvents. HEP solutions of polymers, unlike THF solutions, were always highly diluted (well below 1%), in order to suppress any possible intermolecular interaction between the OH end groups.

Unsaturation

In Figure 3, full-scale IR spectra of a starting low-molar-mass, hydroxyl-telechelic polybutadiene (sample PB-1) and of its hydrogenated analog are given, with both of them measured without any solvent. It can be seen that, after the hydrogenation, all bands pertaining to C=C bonds disappeared as follows: the four strong bands at 910, 968, 995, and 1640 cm^{-1} and a weaker band, pertaining to a combination (overtone) frequency, at 1827 cm^{-1}.
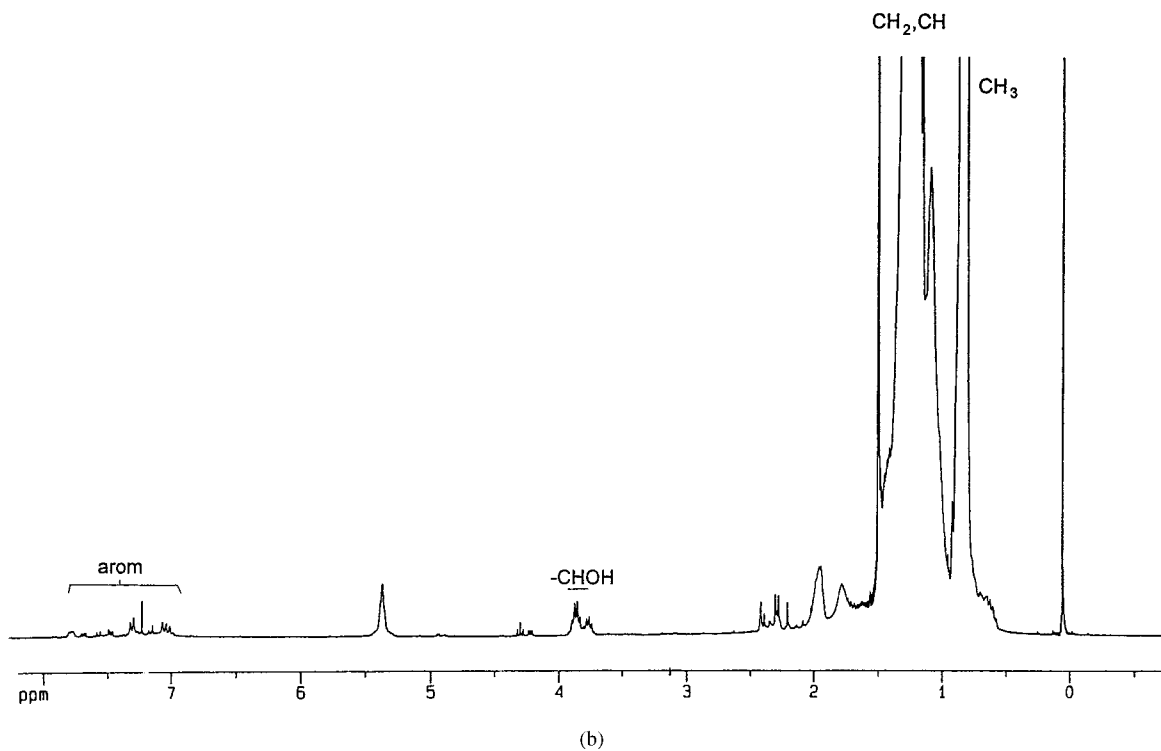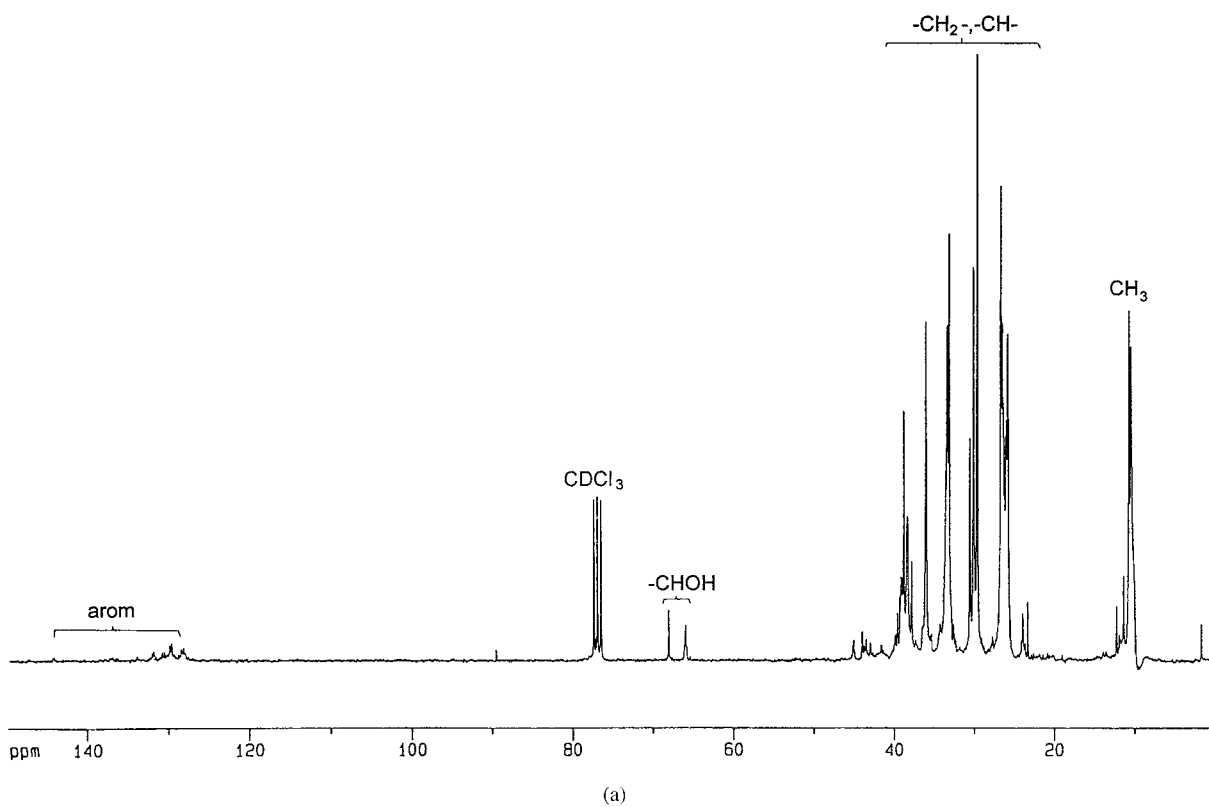
Figure 2 (a) 75.5-MHz ^{13}C-NMR spectrum and (b) 300.1-MHz ^{1}H NMR spectrum of the sample H-2 in CDCl$_3$ at ambient temperature.

Figure 3   FTIR spectra of the samples PB-1 and HPB in heptane at ambient temperature.

The high degree of hydrogenation can even more lucidly be recognized in the Raman spectra (its detail is given in Fig. 4), which were always measured without solvent. For sample PB-1, two strong bands at 1640 and 1666 cm^{-1} are seen, corresponding to the stretching vibration of the C=C bonds of the 1,2 isomer and of the 1,4-*trans* isomer of the butadiene unit, respectively, in accordance with published data.[10] (A band pertaining to the C=C bond of 1,4-*cis* isomer lies most probably in between the two bands, being overlapped by them.) In the same region of wave numbers, the hydrogenated analog shows a smooth baseline only, but a new peak appears at 1597 cm^{-1}, which is missing in the Raman spectra of PB-1; this peak is assigned to the aromatic carbon—carbon bond of the aromatic, sulfur-containing contaminants/substituents, introduced to the polymer by the diimide hydrogenation procedure.[4]

For the determination of the degree of hydrogenation (or, complementary, unsaturation), however, ^{1}H-NMR was used instead of IR or Raman spectroscopy.

Determination of OH End Groups by IR Spectroscopy

Measurements in Heptane. In HEP, the bands of hydroxyl groups appear in the range of approxi-

mately 3500 to 3700 cm^{-1} [Fig. 5(a)]. In this non-polar solvent, it is necessary to dilute the polymer enough to prevent the formation of the intermolecular H-bonds between the hydroxyls.

A comparison between PB and HPB is given in Figure 5(a). The strongest band at 3633 cm^{-1} was assigned to the O—H stretching in the secondary hydroxyl end group —CH(CH$_3$)—OH and is present both before and after hydrogenation. The band at 3597 cm^{-1}, which disappears after hydrogenation, corresponds to a combination frequency of the C=C stretching.

The small inflection (shoulder) at 3611 cm^{-1}, which is present in both spectra in Figure 5(a), pertains most probably to the phenolic OH group of the Irganox 1520 D antioxidant used, as was proved by a comparison with its spectrum (it is not given here).

A new, rather broad band appears in the spectra of HPBs (that is, after hydrogenation) in the range between 3525 and 3575 cm^{-1}, as illustrated in Figure 5(a). Hypothetically, assuming the existence of polymer rings of the following type,
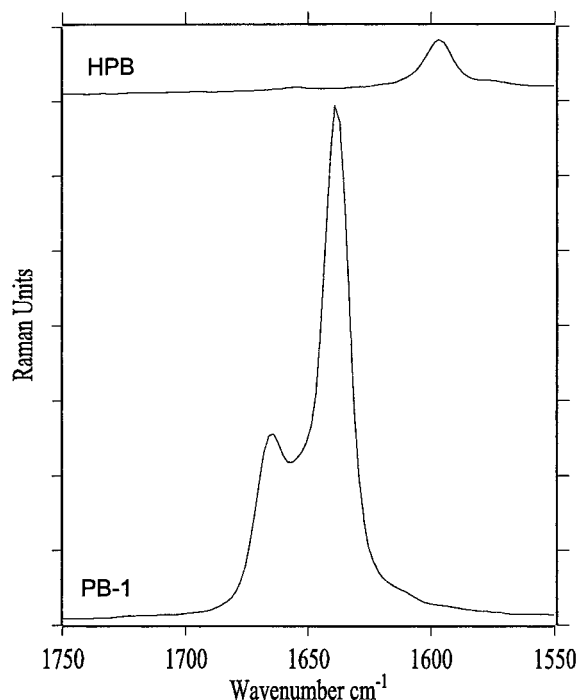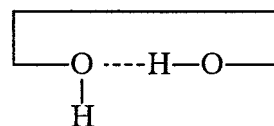
Figure 4   A detail of FT Raman spectra of the samples PB-1 and HPB, measured in bulk at ambient temperature.
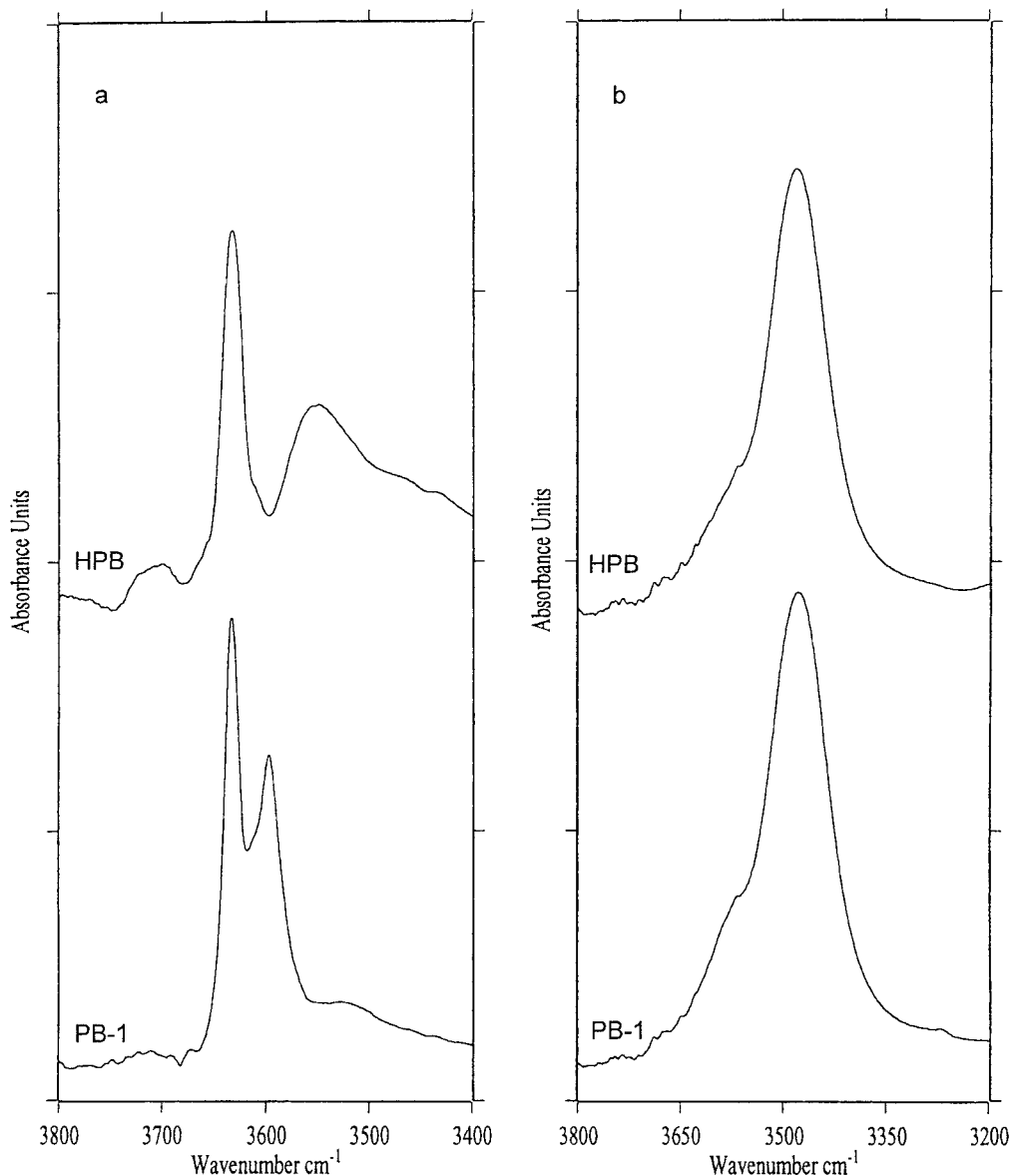
Figure 5 A detail of FTIR spectra of the samples PB-1 and HPB, measured in (a) heptane and (b) THF at ambient temperature.

intramolecular hydroxyl-hydroxyl H-bonds might be responsible for the frequency shifts of the O—H stretching vibrations, but we have no unequivocal explanation for the fact that this band is absent in PBs. Actually, one would expect the opposite. It has been known[11] for a long time that the chains of polybutadienes with high content of 1,4 structural units become (rather paradoxically) more rigid after hydrogenation (i.e., 1,4 polybutadiene is more flexible than the corresponding polyethylene) so that the probability of the formation of such rings would de-

crease. It is possible, however, that the relatively high content of 1,2 units in our PBs (more than 60%) reverses the effect; that is, that the chain stiffness after hydrogenation decreases, but giving a proof would be out of the scope of the present article.

It can be concluded that due to the problems with overlapping the bands and formation of hydrogen bonds, HEP is not a proper solvent for the IR determination of OH end groups. On the other hand, it offers a possibility to study intramolecular H-bonding.

Table II   Values of the Integrated Extinction Coefficient ε ($cm^{-2} \times L \times mol^{-1}$, Measured in THF) of the IR Band of the Secondary Hydroxyl (at ca. 3480 cm^{-1}) of Low-Molar-Mass Alcohols Modeling the Chain Ends of PB and HPB
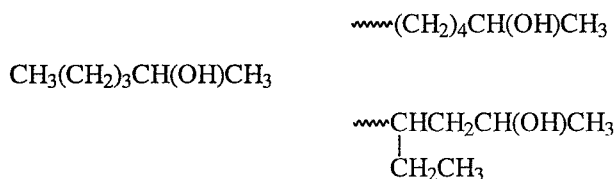
Unsaturated Model	ε	Saturated Analog	ε
5-hexen-2-ol	14,700	2-hexanol	14,000
4-penten-2-ol	13,600	2-pentanol	13,400
—	—	2-butanol	13,500

Measurements in THF. A comparison of the spectra of polymers before and after hydrogenation in HEP and THF are also presented in Figure 5. In THF [Fig. 5(b)], the band of the secondary hydroxyl (at 3480 cm^{-1}) is relatively well resolved, and no band pertaining to the intramolecular H-bonds mentioned above is present in the spectrum any more. In this way, the use of THF enabled us to measure IR spectra with much higher concentrations of polymer and, thus, get a better precision.

A model study was performed in order to get extinction coefficients ε (as measured in THF) of IR bands of several members of a homological series of secondary alcohols, modeling the end of the polymer chain of our PBs, as well as HPBs. Here, the effect of presence/absence of the C=C bond, as well as of the distance between OH and C=C groups, on the value of ε was studied. Results are given in Table II. Of the commercially available alcohols, 5-hexen-2-ol and its saturated analog, 2-hexanol, resemble the real polymer the best. The former substance simulates the end of the chain of PB; the latter, of HPB. 5-Hexen-2-ol corresponds to both 1,4- and 1,2-isomers of the ultimate monomer unit of PB, as follows:

CH₂=CHCH₂CH₂CH(OH)CH₃

〜〜CH=CHCH₂CH₂CH(OH)CH₃

〜〜CHCH₂CH(OH)CH₃
|
CH=CH₂
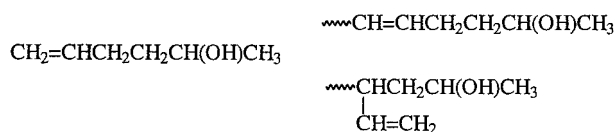
2-Hexanol corresponds to both isomers of the ultimate monomer unit of HPB, as follows:

CH₃(CH₂)₃CH(OH)CH₃

〜〜(CH₂)₄CH(OH)CH₃

〜〜CHCH₂CH(OH)CH₃
|
CH₂CH₃

If a simpler model is used, having only one CH₂ group (instead of two) between C=C and CH(OH), that is, 4-penten-2-ol and its saturated analog, 2-pentanol, then ε decreases by 7 and 4%, respectively (Table II). Further reduction of the number of CH₂ groups is possible in the saturated series only; thus, we get 2-butanol, but this step means no more change of ε. If the relative experimental error of ε is taken into account (ca. 1–2%), it can be concluded that the position of the C=C bond with respect to the OH group is negligible. The effect of saturation of the C=C bond is not large either, but it should be respected; by hydrogenating 5-hexen-2-ol and 4-penten-2-ol, ε drops by 5 and 1.5%.

It was therefore assumed that ε of the hydroxyl IR band of real PB is under given conditions equal to that of 5-hexen-2-ol, that is, 14,700 $cm^{-2} \times L \times mol^{-1}$, while that of real HPB is equal to that of 2-hexanol, that is, 14,000 $cm^{-2} \times L \times mol^{-1}$. Accordingly, the concentration of OH groups in an unknown PB or HPB sample (in mmol/g) was calculated using the following equation:

$$c_{OH} = 10^3 A/(\varepsilon l w_{pol}\rho), \qquad (6)$$

where one of the above values was substituted for ε (according to the nature of the polymer). A, l, w_{pol}, and ρ, respectively, are the measured absorbance of the hydroxyl band, the length of the measuring cell (in cm), the mass fraction of polymer in the solution, and the density of THF (in g $\times$ cm^{-3}). The results are presented in Table I and discussed, together with those of NMR. Each of the c_{OH} values represents an average from several measurements with a reproducibility of about 5%.

Comparison between NMR, IR, and Titrations

For the sake of comparison, both between the methods and between the samples, all values of c_{OH} from Table I were converted into the values of f_{OH} using eq. (1) and listed in Table III. In this way, the effect of molar mass is eliminated. (For the values of molar mass of the PB samples, see the experimental section; by total hydrogenation, molar mass increases by some 4%.)

It follows from Table III that the differences between individual methods are usually not higher than the experimental error, which could be expected for the given range of dilution of OH groups. If the values of f_{OH} for one and the same sample are arranged in decreasing order according to the method of determination, one obtains,

Table III   OH-Functionality f_{OH} of Samples of Polybutadienes Krasol LBH (PB-1 to PB-3) and their Hydrogenated Derivatives (H-1 to H-9), as Determined by Spectroscopic and Titration Methods and Calculated by Eq. (1)

Sample Code	$10^{-3} \times M_n$	^{13}C NMR	^{1}H NMR	IR	Titration
PB-1	2.31[c]	1.48	1.48	1.85	1.77
H-1[a]	2.40[d]	—	1.39	1.65	—
H-2[a]	2.40[d]	1.82	1.53	1.82	1.58
PB-2	3.29[c]	2.14	1.74	2.47	1.94
H-3[b]	3.41[d]	2.22	1.77	2.32	—
H-4[b]	3.41[d]	—	1.64	1.91	—
H-5[b]	3.41[d]	2.05	1.98	1.91	—
H-6[b]	3.41[d]	1.88	1.71	1.98	—
H-7[b]	3.41[d]	—	2.05	1.98	—
H-8[a]	3.41[d]	—	1.57	1.91	—
H-9[a]	3.41[d]	—	1.54	1.71	1.54
PB-3	2.60[c]	1.59	1.72	1.87	1.97

H-1 and H-2 were prepared by hydrogenation of PB-1; other samples were prepared by hydrogenation of PB-2.
Products of hydrogenation were purified in the final step by [a]column chromatography or [b]reduction cleavage.
[c] Values declared by the manufacturers.
[d] Calculated for the hydrogenated derivatives from M_n of the corresponding PB (not measured).

with a few exceptions, the following order: IR $\geq$ titration $\approx$ ^{13}C NMR $\geq$ ^{1}H NMR. If spectroscopic methods only are to be compared, then, on average, IR spectroscopy yields results higher by some 8% than those from ^{13}C-NMR; data obtained from ^{13}C-NMR are higher than those from ^{1}H-NMR by approximately 11%. The deviations are probably due to various reasons like, for example, the different treatment of data, the different influence of impurities, and the fact that both NMR methods are absolute while IR is relative. (As described in detail by Podešva and Holler,[4] samples H-1 and H-2 represent the products of two independent hydrogenation runs, with PB-1 as the starting material in both cases; they differ from each other in the way of hydrogenation and purification only. Similarly, samples H-3 through H-9 were prepared by independent hydrogenation runs from a single stock PB sample, that is PB-2.)

The largest deviations can be observed with PB-2 and H-3, especially where IR spectroscopy yielded $f_{OH} > 2$. However, these deviations can also be due, in principle, to the inaccuracy in the determination of M_n of these samples.

On the other hand, for one and the same method, no systematic change of f_{OH} is observed after the hydrogenation of a particular PB. Both the increase and decrease of f_{OH} can be found; the differences, usually not exceeding some 15%, are probably caused by different nature and different concentration of the impurities present in the material before and after hydrogenation.

As far as acetic anhydride titrations are concerned, the main source of errors is a possible presence of such impurities, which are able to react with anhydride in a way similar to that of OH end groups (that is, to bind to or neutralize an additional part of COOH groups). Since this determination relies on back titration (anhydride is added in excess), such impurities decrease the value of V in eq. (2), thus seemingly increasing the value of c_{OH}. Another disadvantage of these titrations is that the consumption of the sample is by two orders of magnitude higher than with the spectroscopic methods under study.

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