Hydrogenation of Low Molar Mass OH-Telechelic Polybutadienes Catalyzed by Homogeneous Ziegler Nickel Catalysts

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ABSTRACT: Two types of low molar mass, medium vinylic polybutadienes containing 2-hydroxypropyl and 2-hydroxyethyl end groups were hydrogenated in the presence of several homogeneous Ziegler Ni catalysts prepared by using $Ni(acac)_2$ and Ni(2-ethyl-hexanoate)$_2$ as metal precursors and BuLi, Li adduct to a diene and Et_3Al as activators. The catalytic efficiency of these systems determined by rate measurements showed that the best results can be achieved with the Ni(2-hexanoate)$_2$ + Li-diene (Ni : Li mol ratio = 1 : 8–10) catalyst in the solvents commonly used in the synthesis of these polyalkadienes by anionic polymerization of 1,3-butadiene. As found by the kinetic study, the hydrogenation carried out under mild reaction conditions (temperatures of 10–35°C, hydrogen pressure of 72–178 kPa, Ni concentration of 2.1–10.0 mmol/dm^{-3}) was the first order in the OH-polybutadiene and hydrogen and, over narrow range of catalyst concentrations (4.3–10.0 mmol Ni/dm^{-3}), also in the catalyst. The activation energy of the hydrogenation estimated from the Arrhenius plot was 42 kJ/mol. Changes in the relative proportion of 1,2-, *cis*-1,4-, and *trans*-1,4-C=C units of the polymer during hydrogenation indicate the selectivity of the catalyst to the 1,2-hydrogenation. The ease of the addition of hydrogen to the internal C=C unsaturation was found to be opposite to that usually observed (*trans* > *cis*). The present low-pressure hydrogenation of both types of telechelic OH-polybutadienes proceeds with full retention of the average OH functionality and affords the saturated polymers, the residual C=C unsaturation of which (<1%) has so far been usually achieved by high-pressure hydrogenations. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 85: 1185–1193, 2002

Key words: telechelic polybutadienes; hydroxyl end groups; homogeneous hydrogenation; hydrogenation kinetics; Ziegler nickel hydrogenation catalysts

INTRODUCTION

Low molar mass polyalkadienes terminated by hydroxyl groups have found use in several areas of specialty materials,[1] among others as intermediates for the production of special types of polyurethane elastomers (for a recent survey of Czech products, see ref. [2]). However, because of their C=C unsaturation, these polyalkadiene diols are prone to degradation by undesired oxidation and crosslinking reactions. Several hydrogenation methods were used to saturate the polymers on the basis of a stoichiometric reaction with diazene (cf. ref. [3] and references therein) or, more fre-

quently, on a catalytic hydrogenation with gaseous hydrogen.[4]

The common heterogeneous catalysts [Pd/C,[5–7] Pd/alumina,[8] (Pd/C + Ni/silica),[9] Ru/C,[5,7,10,11] Rh/C,[7] Ru/alumina,[5] Ni/alumina,[8] Ni/silica,[11] and supported Ni-Zr[12]] as well as several homogeneous metal complex systems such as Ni(2-ethylhexanoate)$_2$ + Et$_3$Al,[13–15] Co(neodecanoate)$_2$ + Et$_3$Al,[16–18] and RhCl(PPh$_3$)$_3$[19] were applied for this purpose with various success. Thus, for example, the heterogeneous pressure hydrogenation of hydroxylated polybutadienes and polyisoprenes catalyzed in solution by Pd/C and Rh/C was accompanied by splitting off the polymer hydroxyl groups and thus by some loss of their average OH functionality. In the case of the Pd/C catalyst, the mentioned undesired process was suppressed when it was used in a mixture with Ni/silica as a cocatalyst.[11] The selective C=C bond hydrogenation was effected with Ru/C[5] and Ru/alumina,[5] whereas Ni/alumina catalyst was ineffective[8] even on using hydrogen pressures of around 6 MPa.

The results obtained in the hydrogenation of telechelic polybutadiene diols catalyzed by the Wilkinson catalyst [RhCl(PPh$_3$)$_3$] showed that relatively mild conditions used in this case (temperatures around 40°C and moderate hydrogen pressures) did not fully suppress OH-splitting (elimination) reaction.[19] In contradistinction to Ziegler Ni-Al catalysts,[14,15] where no precautions to retain OH functionality seem to have been taken (ca. 6.5 MPa, 95°C, 99% C=C conversion), in the case of analogous Co catalysts,[16] the OH groups had to be protected by acetylation before hydrogenation.

Homogeneously catalyzed hydrogenation has proved to be the method of choice for C=C bond saturation in these polymers. Nevertheless, except for the Rh-catalyzed hydrogenation of telechelic OH-polybutadienes, the kinetics of which was studied,[19] and compared with analogous hydrogenation of the parent (unsubstituted) polymers,[20,21] data on the other catalysts are scarce and incomplete in this respect.

This fact and our previous experience with Ziegler Ni hydrogenation catalysts (cf. refs. [22–25]) led us to test these systems in the above reaction with the following aims:

(1) to compare quantitatively the catalytic efficiency of different Ni catalysts;
(2) to evaluate the effect of solvents and type of polymer OH end groups on the rate of hydrogenation;

(3) to determine kinetics and activation parameters of the reaction;
(4) to evaluate changes in the microstructure and OH functionality of the polybutadienes; and finally
(5) to find conditions under which the hydrogenation affords the saturated polymers with retained OH functionality and minimum residual C=C unsaturation.

For this purpose, we have used two samples of low molar mass, medium vinylic OH-terminated telechelic polybutadienes of similar microstructure that differed in the type of end OH groups [one was a commercial product containing —CH$_2$C(OH)CH$_3$ (secondary OH) end groups (further referred to as sample LBH-1) and the other was a laboratory sample containing terminal —CH$_2$CH$_2$OH (primary OH) groups (LBH-2)]. Both were prepared by anionic polymerization of l,3-butadiene followed by termination of living chain ends with propylene oxide and ethylene oxide, respectively.

EXPERIMENTAL

Materials

Two samples of OH-telechelic polybutadienes were used: a commercial product, Krasol LBH, produced by Kaučuk Group AS (Kralupy n. Vlt., Czech Republic), further referred to as LBH-1. The following parameters were given by the manufacturer: number-average molar mass (M_n) of 3290 g/mol, mass-average molar mass (M_w) of 3750 g/mol, average concentration of the OH groups in the bulk polymer of 0.589 mmol/g, which corresponds to an average OH functionality, f(OH), of 1.94. The sample prepared by anionic polymerization contained 2-hydroxypropyl end groups and its isomeric composition was 60% 1,2-, 15% 1,4-*cis*, and 25% l,4-*trans* C=C units. The other sample (LBH-2) was prepared in the Research Institute, Kaučuk Group AS (Kralupy n.Vlt., Czech Republic), and had the following properties: M_n = 2981, M_w = 3339, fOH = 1.92, 2-hydroxyethyl end groups, 67.3% 1,2-, 11.4% 1,4-*cis*, and 21.3% 1,4-*trans* unsaturation.

Solvents

Cyclohexane, decane, methyl *tert*-butyl ether (MTBE), tetrahydrofuran (THF), and toluene (all

Table I Effect of Catalyst Precursors and Solvents on the Rate of Hydrogenation of LBH-2 (35°C, 122 kPa H$_2$, 0.36 mol dm^{-3} LBH-2)

Ni salt (mmol dm^{-3})	Organometal compound	Solvent	k_1 (min^{-1})
Ni(2-ethylhexanoate)$_2$ (0.43)	Li-diene (4.3)	Cyclohexane	0.30
		MTBE	0.35
		THF	0.26
		Toluene, decane	0.32
	n-BuLi (4.3)	Cyclohexane	0.16
		MTBE	0.14
	Et$_3$Al (1.3)	MTBE	0.18
Ni(acac)$_2$ (0.86)	Li-diene (8.6)	MTBE	0.20
	Et$_3$Al (2.6)	MTBE	0.12
	n-BuLi (8.6)	MTBE	0.08

chemical purity grade; purchased from Sigma-Aldrich S.R.O., Prague, Czech Republic) were dried in the usual way and stored under argon.

Organometal Compounds

Nickel(II) acetyl acetonate (95%, Sigma-Aldrich), nickel(II) 2-ethylhexanoate (from laboratory stock, Ni content = 8.6%), butyllithium (1.6M solution in hexanes, Fluka Chemie A. G., Buchs, Switzerland), and triethylaluminum (93%, Sigma-Aldrich) were commercial products used as obtained. A lithium-diene adduct (further referred as Li-diene) was supplied by the Kaučuk Group and its preparation is subject to patent protection.

Procedures

Preparation of Nickel Catalysts

The catalysts were obtained from nickel salts and Li or Al reagents by the procedure worked out by one of us earlier for Ziegler Ni-Al catalysts for fatty acid esters hydrogenation.[25] In a typical example, the weighed amount of Ni(acac)$_2$ was placed into a 50-mL glass vessel which was evacuated and purged with argon. Then, cyclohexane was added under a stream of argon in such an amount as to make Ni concentration equal to 8.6 $\times 10^{-2}$ mol Ni/dm^3. The reaction flask was then fitted with a reflux condenser topped with an argon adapter, and the contents were heated with magnetic stirring to 50°C for 10 min. Then, 10% cyclohexane solution of triethylaluminum was rapidly added in the amount ensuring the Ni : Al molar ratio = 1 : 3. The black mixture so formed was stirred and heated to the above temperature for another 10 min and then was allowed to cool spontaneously to room temperature. To avoid the

eventual changes in the catalytic efficiency of the so prepared stock solutions due to their longer standing on kinetic measurements, they were always prepared fresh for each series of kinetic runs (1-day measurements), and the stability of catalytic behavior (which was well reproducible for each pair of catalyst precursors listed in Table I) was checked by repeating the first run after completion of the whole series of measurements. It was found that the rate data differed from each other within experimental errors of the rate constant determination (15 relative % at maximum).

Kinetic Measurements

Hydrogenation Apparatus. Rate data were obtained with a hydrogenation apparatus working at a constant hydrogen pressure, the scheme of which is shown in Figure 1 (details were reported elsewhere[26]). The time dependence of hydrogen consumption was recorded automatically. The apparatus was allowed to follow hydrogenation at which the rate of hydrogen consumption did not exceed 0.7 cm^3 s^{-1}.

Procedure. The hydrogenation reactor, equipped with a side arm topped with a septum, was connected to the hydrogenation apparatus via screw-thread plastic connector. The whole system was evacuated and thrice filled with hydrogen (that was passed over a palladium catalyst to remove traces of oxygen and through a molecular sieve to capture the gas moisture). Then, solvent and substrate solution were subsequently injected into the reactor through the septum via dry hypodermic syringes and the magnetically stirred mixture was warmed up to the reaction temperature. The hydrogenation was started by adding the cat-
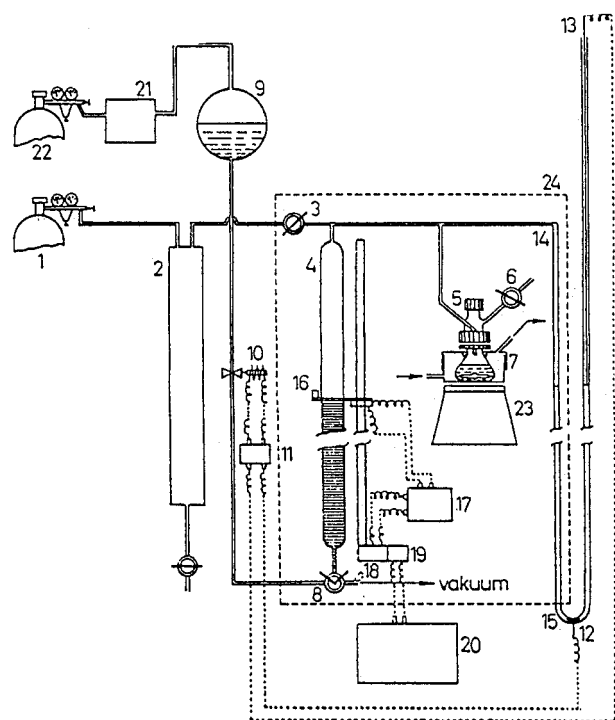
Figure 1 Scheme of hydrogenation apparatus. Pressure range: maximum, 0.2 MPa; maximum rate of gas consumption, 0.7 cm^3 s^{-1}. (1) Hydrogen pressure tank; (2) purification unit; (3) stopcock; (4) gas burette (250 mL); (5) reactor; (6) and (8) stopcocks; (7) thermostatted bath; (9) inert sealing liquid; (10) switching valve; (11) relay; (12) and (13) platinum contacts; (14) U-shaped mercury tube; (15) inert capillary; (16) photoelectric sensor; (17) controlling block; (18) servomechanism; (19) resistance transmitter; (20) strip chart recorder; (21) manostat; (22) argon cylinder.

alyst stock solution and hydrogen consumption was followed photoelectrically and recorded with a strip chart recorder.

Treatment of Kinetic Data. Preliminary experiments showed that the rate of hydrogenation consumption in all runs fits a pseudo-first-order kinetics (hydrogen pressure being kept constant during the experiment). This allowed us to calculate the rate constants of hydrogenation as the slope of the $\ln(V_{00}/V_{00} - V_t)$ versus t linear plot where V_{00} is the volume of hydrogen calculated for 100% C=C bond saturation and V_t is the volume of hydrogen consumed at time t. As with some catalytic systems listed in Table I the rate of hydrogen consumption deviated from the linear plot at later stages of the reaction (in general around its half-time), the rate constants calculated in these cases had been considered as the

initial rate constants and designated k_0, contrary to the rate constants k_1 in Table II, which corresponded to at least two half-time reaction courses.

Preparative Hydrogenations

A series of partially hydrogenated samples LBHH 2–LBHH 9 were prepared with the use of the apparatus used in kinetic measurements but in this case the apparatus was connected to a 250-mL reactor. The hydrogenation was carried out under reaction conditions given in Table III and was always stopped when the volume of the consumed hydrogen corresponded to the required C=C bond conversion. After completion of each partial hydrogenation, the sample was isolated as described in the next paragraph and its microstructure and the average OH functionality were determined by IR spectroscopy and liquid chromatography, respectively.

Isolation Procedure

A liquid reaction mixture after hydrogenation containing about 10 g of partially hydrogenated LBH was placed into a separating funnel. A total of 0.5 mL of 30% hydrogen peroxide was added; the contents were thoroughly shaken, and then a 0.5-mL portion of 85% phosphoric acid was added. After thorough shaking, a greenish precipitate formed was allowed to settle and separate, and the organic layer was washed thrice with 100-mL portions of water. The aqueous layer was discarded, and the polymer solution was added dropwise to a reaction flask placed on an oil bath heated to 160°C to remove solvent as fast as possible. During the solvent evaporation, a stream of argon was led into the flask. The polymer so obtained was stored under argon in vials or stabilized by Irganox 1520 D (0.2%) and stored in the dark at ambient temperature.

Measurements

The microstructure of LBH-1, LBH-2, and the hydrogenated OH-polybutadienes LBHH was determined in the Research Institute of Kaučuk Group by IR spectroscopy; relevant data are listed in Table III. The average OH functionality $f(OH)$ was determined by titration of the OH groups by acetanhydride, and the relative proportions of individual components [i.e., of the unsubstituted polybutadiene, $f(OH)_0$, monohydroxy-terminated polybutadiene, $f(OH)_1$, and telechelic dihydroxy-

Table II   Rate Data on Hydrogenation of LBH-2 (0.36 mol/dm^3) Catalyzed by Ni(2-Ethylhexanoate)$_2$ + Li-Diene in MTBE

No.	Ni (mmol/dm^3)	Ni/Al (mol ratio)	t (°C)	pH$_2$ (kPa)	k_1 (min^{-1})
1	4.3	1 : 4	25	125	0.01
2	4.3	1 : 6	25	125	0.09
3	4.3	1 : 8	25	125	0.16
4	4.3	1 : 10	25	125	0.16
5	4.3	1 : 12	25	125	0.14
6	4.3	1 : 8	25	72	0.10
7	4.3	1 : 8	25	99	0.14
8	4.3	1 : 8	25	152	0.20
9	4.3	1 : 8	25	178	0.25
10	4.3	1 : 8	15	125	0.08
11	4.3	1 : 8	20	125	0.10
12	4.3	1 : 8	30	125	0.19
13	4.3	1 : 8	35	125	0.25
14	2.1	1 : 8	35	125	0.06
15	3.3	1 : 8	35	125	0.15
16	5.3	1 : 8	35	125	0.33
17	8.6	1 : 8	35	125	0.52
18	10.0	1 : 8	35	125	0.62

polybutadiene, f(OH)$_2$] were determined by liquid chromatography.[27]

RESULTS AND DISCUSSION

Effect of Solvents, Nickel Precursors, and Organometal Compounds

Ziegler-type catalysts are in general prepared by the reaction of a suitable transition metal salt

Table III   Changes in Microstructure During Hydrogenation of LBH-2 in MTBE at 25°C

Sample	Hydrogenation (%)	C=C (rel. %)		
		1,2-	*cis*-1,4-	*trans*-1,4-
LBH-2	0	67.3	11.4	21.3
LBHH-1	15	62.0	14.2	23.8
LBHH-2	30	55.5	17.1	27.4
LBHH-3	45	44.1	21.0	34.9
LBHH-4	55	37.3	23.9	38.8
LBHH-5	60	27.7	30.0	42.3
LBHH-6	70	13.8	56.9	29.2
LBHH-7	80	3.8	71.7	24.5
LBHH-8	90	0.5	79.3	20.2

LBH-2 0.36 mol/dm^3, Ni(2-ethylhexanoate)$_2$ (4.3 mmol/dm^3) + Li-diene (Ni : Li = 1 : 8), pH$_2$ = 125 kPa.

with organoaluminum or organolithium compounds. However, in addition to the structure of these substances, the final properties of such catalysts are strongly affected by several reaction parameters, especially by the molar ratio of both components and by the temperature and way of catalyst formation (less also by solvent), so that preliminary experiments are usually needed to find optimum conditions for the case under study.

For that reason, and with the aim of making an intended comparison of the efficiency of Ni catalysts obtained from different metal salt–organometal compound pairs shown in Table I meaningful, in preparatory experiments we have tested the effect of the above parameters for each pair separately. The results of these tests showed that they are best prepared by the procedure used earlier by one of us in the study of hydrogenation of fatty acid esters.[25] The most active catalysts (measured by hydrogenation rate) of sufficient stability (no changes in activity on standing for 2 days) were obtained with the metal to organometal compound molar ratios given in Table I.

It was found that during hydrogenation of LBH-2 the rate of hydrogen consumption follows with all the catalysts the first-order kinetics at least to one-half time. This made it possible to compare the activity of these Ni systems quantitatively on the basis of the corresponding pseudo-
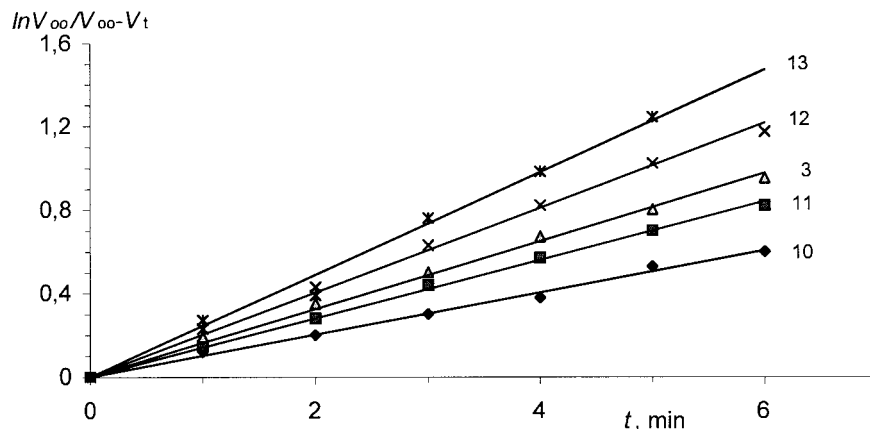
Figure 2   Effect of hydrogen pressure on time dependence of $\ln V_{00}/V_{00} - V_t$ of LBH-2 hydrogenation (experiments 3, 6–8, Table II). Hydrogen pressure: (1) 72 kPa; (2) 99 kPa; (3) 125 kPa; (4) 152 kPa; (5) 178 kPa.

first-order rate constants k_0. The results summarized in Table I show that at least in the case under study:

1. Ni(2-ethylhexanoate)$_2$ is the better metal precursor than Ni(acac)$_2$, irrespective of the kind of organometal compound used;
2. Li-diene adduct affords the more active catalyst systems than n-BuLi and Et$_3$Al, the latter in turn being comparable to each other;
3. the solvents used to produce unsaturated telechelic OH polymers (THF, cyclohexane, MTBE) can all be used as a medium in their hydrogenation.

Its worth mentioning that similar results (not included in this article) were obtained with LBH-1, too, in harmony with the similar structure and the expected insignificant role of end OH groups on the course of the hydrogenation.

Kinetics of Hydrogenation

On the basis of similar kinetic patterns observed for the Ni systems described above, a more detailed study of kinetics of the hydrogenation was performed with the following model system: the substrate LBH-2, the solvent MTBE, and Ni(2-ethylhexanoate)$_2$ + Li-alkadiene as the catalyst. The effect of the following kinetic parameters was examined: the pressure of hydrogen, the initial concentration of the hydrogenation catalyst, and temperature. Rate measurements were carried out on a hydrogenation apparatus working at a

constant hydrogen pressure. The equipment was connected to an automatic recording of the time dependence of the volume of hydrogen consumed by the reaction with C=C bonds of the polymer (for the scheme and hydrogenation procedure, see Experimental). The concentration of LBH-2 in MTBE was used low enough (0.36 mol/dm^3) to safely eliminate mass transfer effects and to ensure that the rate measurements are carried out in kinetic region (magnetic stirrer 1350 rpm).

The pseudo-first-order rate constants k_1 (min^{-1}) calculated as the slopes of the $\ln(V_{00}/V_{00} - V_t)$ versus time t dependences are summarized in Table II, and, as an example, the corresponding plots obtained from experimental V_t versus t curves are shown in Figures 2 and 5. It is seen that in most experiments the course of the hydrogenation at a constant hydrogen pressure fits the first-order kinetic relation up to the late stages of the hydrogenation (i.e., to the high C=C bond conversions), which also documents that the reaction is the first order in the telechelic polymer LBH-2.

The linear dependence of k_1 on hydrogen pressure (Fig. 3) speaks for the first order in hydrogen, at least in the region of hydrogen pressures tested (72–178 kPa).

As shown in Figure 4, the effect of the catalyst concentration on the rate data is not so clear cut. We believe that, due to the nonuniform nature of species in the Ziegler-type systems, the observed deviation from the first-order correlation (found to hold for 4.3–10 mmol/dm^3 Ni concentration) on going to lower initial catalyst concentrations is more likely caused by deactivation of a certain
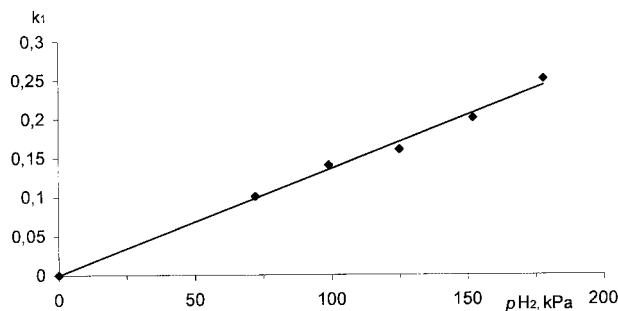
Figure 3 Dependence of the rate constant k_1 (min^{-1}) of LBH-2 hydrogenation on hydrogen pressure pH$_2$ (Pa) (k_1 values calculated as the slopes of the dependences in Fig. 2 are given in Table I, Nos. 3, 6–8).

part of the catalytically active Ni species rather than by the uniform deactivation of the whole system. It is worth mentioning that the pseudo-first-order kinetics is obeyed here only in the initial phase of the hydrogenation and at these catalyst concentrations the catalyst is subject to further deactivation during hydrogenation.

Finally, the effect of temperature on the reaction rate was examined to determine the activation energy of the reaction. To obtain data for the Arrhenius plot, kinetic measurements were carried out over the range of 15–35°C. The corresponding rate constants k_1 obtained as the slopes of the dependences shown in Figure 5 are listed in Table II (experiments 3, 10–13). The activation energy E_0 estimated from the slope of the least-squared Arrhenius plot (Fig. 6) is 42 kJ mol^{-1}. At present, no relevant data are available for comparison with other homogeneously catalyzed hydrogenations of telechelic OH-polybutadienes, as with RhCl(PPh$_3$)$_3$ (the only catalyst so far stud-

ied), the log k versus $1/T$ correlation had not been linear, due to the additive character of the rate constant resulting from a multistep reaction mechanism.[19]

Changes in Microstructure and OH Functionality of LBH Polymers During Hydrogenation

The samples of OH-telechelic polybutadienes chosen as model compounds (LBH-1 and LBH-2) in the present study contained both terminal (1,2-) and chain (*cis*- and *trans*-l,4-) C=C unsaturation. As 1,2- and 1,4-C=C units show different reactivities toward chemical modification reactions[4] (the terminal units 1,2- are usually more reactive because of their lower steric hindrance), it was of interest to determine how the selectivity of terminal versus internal C=C hydrogenation is affected by the catalysts under study. Because of the already mentioned similar microstructure of both samples, changes in the polymer microstructure during hydrogenation were examined in detail only with the use of LBH-2 in MTBE solution, using Ni(2-ethylhexanoate)$_2$ + Li-diene (Ni : Li mol. ratio = l : 10) as the catalyst.

The relative proportion of the isomeric C=C units in dependence on the degree of the polymer saturation (for 15–90% hydrogenation) are presented in Table III. In Figure 7, these data are converted to the actual content of individual units in the given partially hydrogenated samples and plotted against the degree of the hydrogenation of the sample. It is seen that up to ~ 60% hydrogenation, practically the only C=C units undergoing reaction with hydrogen, are the vinyl groups (1,2-). At further stages, all are hydrogenated at a rate that seems to decrease in the order l,2- > *trans*-1,4 > *cis*-1,4.
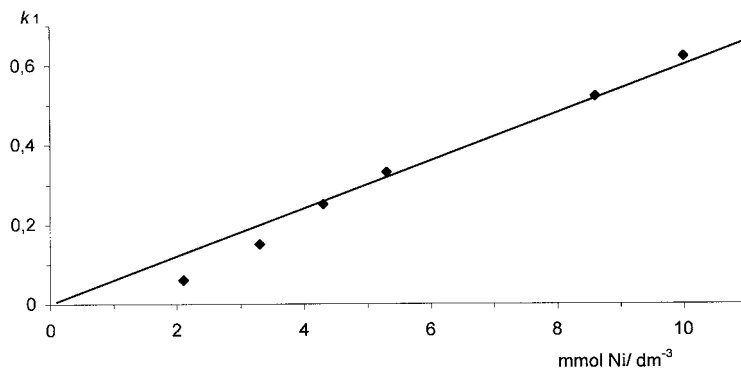

Figure 4 Dependence of the rate constant k_1 (min^{-1}) of LBH-2 hydrogenation on total Ni concentration (mmol dm^{-3}) (Table I, experiments 13–18). The line calculated by the least-squares method; the first two points not included.
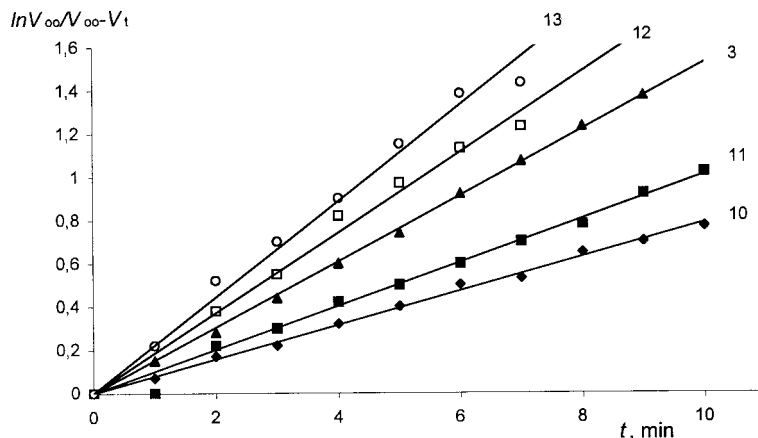
Figure 5 Effect of temperature on time dependence of ln $V_{00}/V_{00} - V_t$ of LBH-2 hydrogenation (experiments 3, 10–13, Table II). (1) 15°C; (2) 20°C; (3) 25°C; (4) 30°C; and (5) 35°C.

In light of the greater accessibility of the C=C bond in the *cis* than *trans* arrangement, the reverse reactivity order deduced from the above data is surprising. No reason can be offered at present to account for this finding. Further experiments with the polymers containing the greater internal C=C unsaturation are underway to deal with this problem.

As already mentioned, the undesired side reaction in the hydrogenation of polyalkadienes containing hydroxyl groups is the C—OH fission. Although in the case of polyhydroxylated polymers containing pendant OH groups, some loss of their OH functionality can be tolerated, with telechelic diols such a loss might be detrimental for some applications.

The following results [average OH functionality, f(OH)] were obtained for LBH-1 and LBH-2 by

their total hydrogenation (degree of hydrogenation is given in parentheses) under the conditions given in Table II, experiment 16:

Sample	LBH-1	LBH-1 (98,8%)	LBH-2	LBH-2 (99.2%)
f(OH)	1.94	1.95	1.92	1.94

The data document that the initial OH functionality of the polymers is retained [the slight f(OH) increase is due to separation of the part of the unsubstituted polybutadiene from the sample during its isolation; for procedure, see Experimental].

The low residual unsaturation of both hydrogenated samples speaks for the high efficiency of
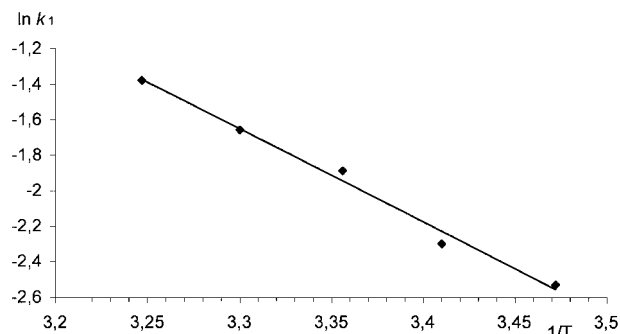

Figure 6 The Arrhenius plot for LBH-2 hydrogenation (k_1 values calculated as the slopes of the dependences in Fig. 5 are listed in Table I, experiments 3, 10–13).
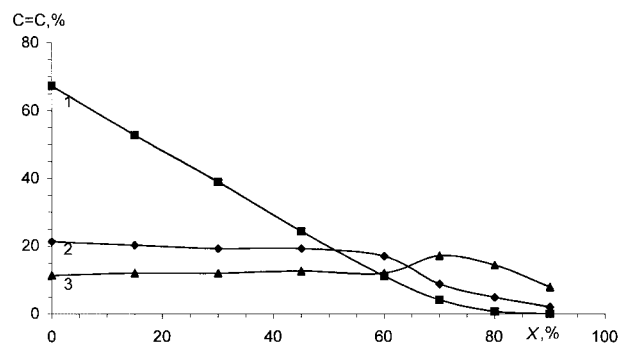

Figure 7 Changes in the content of 1,2- (curve 1), *trans*-1,4 (curve 2), and *cis*-1,4- (curve 3) C=C units (%) of LBH-2 dependence on the extent of its hydrogenation (total C=C conversion X, %) at 25°C (for reaction conditions, see experiment 4, Table II).

the catalyst system. In this respect, the hydrogenation affords the saturated products with the residual unsaturation achieved by homogeneous Ziegler Ni (cf. refs. [15,28]) or Co (cf. refs. [16–18]) catalysts so far by high-pressure hydrogenations.

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