Hydrogenation of Low-Molar-Mass, OH-Telechelic Polybutadienes. I. Methods Based on Diimide

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Received 16 June 1998; accepted 22 May 1999

ABSTRACT: Low-molar-mass, OH-telechelic polybutadienes were hydrogenated (1) by diimide alone and (2) by using a novel method, consisting of the following two steps: up to some 95% degree of conversion by gaseous hydrogen with conventional Ziegler–Natta catalysts, and, only then, up to almost full saturation by diimide. The two-step method, which has been found to be equally efficient, enables one to decrease substantially the necessary feed of *p*-toluenesulfonylhydrazide, by the thermal decomposition of which diimide is generated. The crude saturated products, which could not be purified by a conventional (re)precipitation technique due to their low molar mass, contained a relatively large amount of a side-product, bis(*p*-tolyl)disulfide (TDS). It was found that free TDS can be converted quantitatively by reduction cleavage into *p*-tolyl mercaptan (TM) without changing the structure of the polymeric product, and TM can then be removed from the mixture by alkaline extraction. Alternatively, the crude product can be freed from TDS by chromatography. With the two-step hydrogenation method, only a small amount of the fragments and/or precursors of TDS add to the 5% residual C═C double bonds of the partially hydrogenated polybutadiene chains. After any of the two purification procedures, the fully saturated products usually contained less than 1 wt % of such undesirable substituents only, which is comparable with the reported single-step diimide hydrogenation of the initial, fully unsaturated polybutadiene in the presence of a proton scavenger (tri-*n*-propylamine). © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 3203–3213, 1999

Key words: hydroxyl-telechelic polybutadienes; diimide; *p*-toluenesulfonylhydrazide; bis(*p*-tolyl)disulfide; *p*-tolyl mercaptan; tri-*n*-propylamine; hydrogenation

INTRODUCTION

Classical catalytic hydrogenations of polydienes by gaseous hydrogen are usually not quantitative when common heterogeneous catalysts are used and are often quite expansive when homogeneous, metal-based catalysis is applied (in the latter case, the catalyst gets sometimes bound chemically to the chain and cannot, therefore, be regenerated; moreover, the product can thus be irreversibly colored).

A relatively novel hydrogenation method is based on the reaction between an olefinic bond (be it in the pending vinyl group or in the main chain) and diimide (diazene, N_2H_2).[1–3] Hydrogen atoms of diimide add to the double bond, diimide decomposes, and N_2 is released.

$$\sim\!\!\sim CH{=}CH\sim\!\!\sim + N_2H_2 \rightarrow \sim\!\!\sim CH_2{-}CH_2\sim\!\!\sim + N_2 \quad (1)$$

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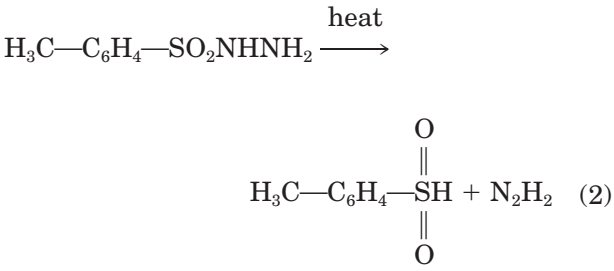
Contract grant sponsor: Grant Agency of the Academy of Sciences of the Czech Republic; contract grant number: A4072902.

Journal of Applied Polymer Science, Vol. 74, 3203–3213 (1999)
 CCC 0021-8995/99/133203-11

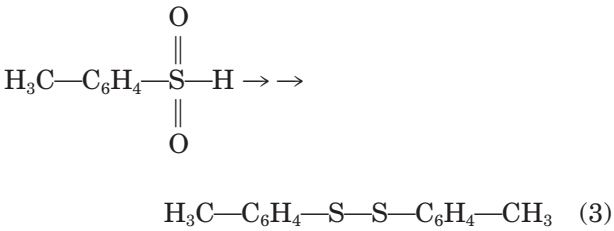
Diimide is an unstable compound which can be generated *in situ* by, for example, thermolysis of *p*-toluenesulfonylhydrazide (TSH),[1,2]



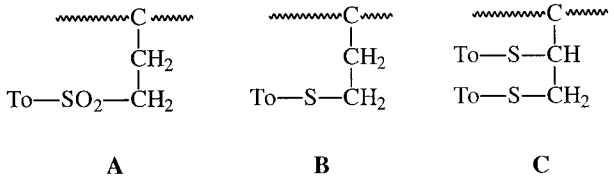
or by oxidation of hydrazine using hydrogen peroxide.[3] (The latter alternative has been described for aqueous dispersions only.)

Diimide, as generated from TSH, is a very effective hydrogenation agent, with which, under favorable conditions, a virtually total saturation of the polydiene substrate can be achieved.[4,5] It is possible to reach such a high degree of conversion that the determination of the residual unsaturation is near the perceivability limit of advanced spectroscopic methods. However, when this is required, TSH, which is a rather expensive substance, must be applied in a relatively high mole excess with respect to the C═C bonds.

Other problems arise from the fact that, in addition to the desirable diimide, also undesirable by-products are formed during the decomposition of TSH. The primary by-product (fragment of TSH) is *p*-toluenesulfinic acid [cf. eq. (2)]. Simultaneously with hydrogenation of the polymer substrate, this acid undergoes a whole cascade of spontaneous subsequent reactions, via several intermediates[6]; and this chain of reactions yields bis(*p*-tolyl)disulfide (TDS),[1,2] which is relatively stable. (Conflicting results have been published, and no systematic study on these side products has been done so far. Some authors reported that the final by-product is *p*-tolyl-*p*-toluenethiolsulfonate[6,7] but it seems that TDS is by far the most predominating contaminant of the hydrogenated polymer product.)



It was soon recognized,[1,2,8] however, that both TDS and its precursor, *p*-toluenesulfinic acid, are able to add to the residual olefinic double bonds of the polydiene during the hydrogenation, preferentially to the pending vinyl groups. For most applications, additions of these sulfur-containing compounds onto the polymer chain are undesirable reactions, potentially competitive to the hydrogenation. Reportedly,[8,9] up to several percent of the polymeric C═C bonds can undergo such an addition. It is assumed[8] that the addition of the acid can be governed by both ionic and free-radical mechanisms, yielding a sulfone (structure **A**, To = *p*-tolyl); whereas the addition of the fragments of TDS (formed by homolytical cleavage of the bond between the sulphur atoms) is governed by a free-radical mechanism only. The authors[8] offer no explanation why they assume that only one sulfidic radical adds onto the C═C bond yielding the structure **B** and where the complementary hydrogen radical is taken from (perhaps from an antioxidant). In our opinion, the existence of the structure **C** (formed by adding both sulfidic radicals) cannot be excluded, either. Again, no systematic study has been published on this addition.



A **B** **C**

Later, methods were developed, which strongly limit the extent of such side reactions. It has been found that the presence of a relatively large amount of an antioxidant in the reacting hydrogenation mixture (in a concentration higher than usual for standard stabilization) suppressed effectively free-radical addition of the fragments of TDS to the C═C bonds of the chain[8]; this also inhibited any possible degradation and/or crosslinking reactions on the polymer chain level.[5] Further, tri-*n*-propylamine (TPA), which is a strong proton acceptor, reportedly blocks the ionic addition of *p*-toluenesulfinic acid to the chain.[9]

Thus, it is possible now to diminish the extent of such additions of the sulfur-containing contaminants onto the chain. However, even if such additions are prevented, the crude polymer product still contains TDS in a free, unbound form; and it is often necessary to remove it. This can be done very easily when medium- and high-molar-mass

polydienes are the substrates to be saturated: standard (re)precipitation procedures (e.g., pouring a benzene solution of the polymer product into excess methanol) can be applied in this case because all impurities mentioned above are soluble in methanol. Serious isolation problems may arise when very low-molar-mass polydienes, such as the so-called liquid rubbers, are hydrogenated. It is well known that when a solution of a polymer having its molar mass below, say, 5000 g/mol is poured into a precipitant, no proper coagulation usually takes place and, instead, stable nonsedimenting emulsions are formed. (The phases of these emulsions can in principle be separated by the centrifugation, but this procedure is usually limited to a small scale.)

One of the aims of the present article was to find proper methods of removing as much contaminants as possible from the product of the diimide hydrogenation, without changing the chemical structure of the polymer (neither on the level of functional groups nor on the level of the chain). We have tried to compare the efficiency of the purification methods tested. Second, we have checked the suitability of a two-step hydrogenation method, combining the advantage of a relatively low-cost of the catalytic prehydrogenation by elemental hydrogen and the high effectivity of the post-hydrogenation by diimide. In the first step, the low-molar-mass, hydroxyl-telechelic polybutadiene (PB) was hydrogenated by H_2 up to the maximum possible level (usually some 95% or slightly more in our case) using a Ziegler–Natta catalyst to yield partially hydrogenated polybutadiene, pHPB; in the second step, the residual double bonds were saturated by TSH up to almost 100% (yielding HPB). Third, we have tried to find out if, even for the 95% hydrogenated polymer intermediate under study, the presence of TPA is necessary for preventing the TSH fragments and/or derivatives from adding to the residual C═C bonds.

EXPERIMENTAL

Materials

Substrates

Two samples of the low-molar-mass, hydroxyl-telechelic polybutadiene (PB-1 and PB-2) were used. They were commercial products by Kaučuk Group AS (Kralupy n. Vlt., Czech Republic), marketed under the trademark Krasol LBH. The following parameters were given by the manufacturer: number-average molar masses of 2310 and 3290 g/mol, and mass-average molar masses of 2610 and 3750 g/mol, respectively; average concentrations of the OH groups in the bulk polymer of 0.765 and 0.589 mmol/g, which corresponds to an average OH functionality of 1.77 and 1.94, respectively; stabilization of both samples, Irganox 1520 D (0.2%); and content of isomeric structures of 60% 1,2, 15% 1,4-cis, and 25% 1,4-trans for both samples (in comparison, we have determined the fraction of the 1,2 structure by ^{1}H nuclear magnetic resonance to be 63.6 and 62.0%, respectively).

To get a third sample for diimide hydrogenations, a portion of PB-2 has been partially hydrogenated by Ni-acetylacetonate/triethyl aluminum system. The resulting intermediate has been denoted as pHPB. This first hydrogenation step was based on a method described earlier[10] but was correspondingly modified. The degree of hydrogenation, as determined by ^{1}H nuclear magnetic resonance (^{1}H-NMR), was 96%. The OH functionality has not changed within the limits of the experimental error.[11]

Hydrogenation Agent

TSH, supplied by Fluka as purum grade, was recrystallized from ethanol and dried *in vacuo* at 50°C for 12 h (106°C mp).

Solvents

Xylene, *n*-hexane, *n*-heptane, *n*-octane, and *n*-decane were used as obtained (*n*-decane from Fluka, as purum grade; others from Lachema, Czech Republic, as p.a. grade). Methyl-*tert*-butyl ether (MTBE) was supplied by Kaučuk Group AS (Kralupy n. Vlt., Czech Republic).

Other Reagents

Tri-*n*-propylamine (TPA) was purchased from Fluka as purum grade and used as received. Bis(*p*-tolyl)disulfide (TDS), used for infrared (IR) spectrometric identification of the low-molar-mass contaminant and for the estimation of the distribution coefficients, was obtained from Sigma-Aldrich. *p*-Tolyl mercaptan (TM), used for the IR identification of the product of the reduction scission of TDS, was supplied by Fluka.

Procedures

Hydrogenations

The polymer intermediate pHPB, having the degree of saturation 96%, was prepared by a

method[10] modified for the PB samples under study (hydrogenations of PB's by the Ziegler–Natta catalysts will be the subject of a forthcoming article[12]). Thus, in a typical run, a three-necked glass reactor (100-mL capacity) equipped with a magnetic stirrer and hydrogen inlet tube was evacuated, purged with hydrogen, and then charged successively with 50 mL of the solvent (MTBE) and 10 mL of the PB solution (22 wt % in MTBE) under stirring. After the temperature of the mixture was raised up to 40°C, 1 mL of 0.08*M* solution of the catalyst prepared separately from nickel acetylacetonate and triethylaluminum (1 : 3 mole ratio) was added. Hydrogen overpressure was adjusted at 1875 kPa and maintained at this value for 30 min. The solvent was then evaporated *in vacuo* from the black reaction mixture, and the residue was redissolved in 50 mL of xylene. After addition of a few drops of water, the catalyst coagulated within several hours to form a black sediment which was filtered off by a paper filter. The clear filtrate (solution of the pHPB in xylene) can be used for the next step (diimide post-hydrogenation) directly, without isolation.

A part of the filtrate was evaporated again, and the residue was tested for the presence of Ni by the atomic absorption spectrometry. The concentration of Ni was found negligible (the difference between the sample and the blank determination was smaller than the experimental error), that is, less than approximately 0.01 mg/L.

As for the diimide step, specific feeds of reaction components for individual hydrogenation runs are given in Table I in the results and discussion. Generally, a polymer substrate (PB-1 or PB-2 or pHPB), additional antioxidant Irganox 1010 [0.1% (*w*/*v*)], and, in some runs, TPA were put in a round-bottom flask, equipped with a mechanical stirrer, reflux condenser, and a three-way stopcock for the inert gas inlet/outlet. The mixture was dissolved in xylene, and the solution was stirred and heated under argon atmosphere up to approximately 100°C. To this hot solution, TSH was added, which dissolved quickly. With continuous stirring under Ar, temperature was increased up to the boiling point of the mixture, which was refluxed for 7 h.

Table I Conditions of the Diimide Hydrogenations

Hydrogenation Run	h_{sub}	[C═C]	[TSH]/[C═C]	[TPA]
H-1[a]	0	0.411	2.00	0
H-2[a]	0	0.264	1.93	0.509
H-3[b]	0	0.286	1.99	0.569
H-4[b]	0	0.555	2.00	1.10
H-5[c]	0.96	0.023	4.96	0
H-6[c]	0.96	0.023	4.98	0
H-7[c]	0.96	0.0144	3.01	0
H-8[c]	0.96	0.0095	4.41	0.043
H-9[c]	0.96	0.0114	6.23	0.071

Hydrogenations were carried out in boiling xylene in the presence of 0.1% (*w*/*v*) Irganox 1010 with [a]PB-1 or [b]PB-2 or [c]pHPB as the starting polymer substrate having the degree of hydrogenation h_{sub}. The symbols [C═C], [TSH], and [TPA] denote mole concentrations (in mol/L) of, respectively, unsaturated monomer units of the polymer substrate, *p*-toluenesulfonylhydrazide, and tri-*n*-propylamine in the initial reaction mixture.

Prepurification Procedure

This stage was the same for all diimide hydrogenation runs. Xylene (and, possibly, also a part of TPA) was evaporated quantitatively *in vacuo* directly from the reaction vessel. To the resulting syrupy or semicrystalline residue, a two-phase mixture of octane and methanol (ca. 1/1 *v*/*v*) was added, and the system was stirred until the residue dissolved. The two-phase solution was then transferred into a separation funnel and vigorously shaken. After the sedimentation of phases, polymer concentrated in the upper, octane-rich phase. The methanol-rich phase, which contained mostly TDS, was separated, and a new portion of methanol was introduced. Formation of an emulsion (which appeared in some cases due to the fact that the polymer with hydroxyl end groups acts as a surfactant) can be suppressed, and the separation of layers can thus be speeded up by addition of approximately 1% (*w*/*v*) $CaCl_2$ to methanol. Methanolic extraction was repeated five times. Finally, the upper phase was filtered through a paper filter, and the solvents were evaporated therefrom, leaving partially purified product, which still contained some free TDS. Due to the presence of this contaminant, the yield was always higher than 100% of theory. The product was divided into the following two parts: one was characterized at this level of contaminants; the other was further purified.

Isolation Procedure

Two alternative methods were developed to remove the remaining free, unbound TDS.

The chromatographic method was performed as follows. The partially purified product (typically 3 g) was dissolved in a small amount of heptane, and the solution was introduced into a simple preparative column packed with silica (12 g; 15-μm grain diameter; 12-nm average porosity; SiO_2-activated at 500°C). Heptane was applied as the initial mobile phase eluting free TDS (and a small amount of another low-molar-mass substance) and leaving polymer on the start; heptane was then substituted by methyl-*tert*-butyl ether, which eluted the polymer component.

In a typical run of the chemical method, the crude product of the diimide hydrogenation (3.3 g) was dissolved in 50 mL of hexane and placed in a 100-mL flask equipped with a magnetic stirrer and a reflux condenser. 0.3 g of Zn powder (a molar excess with respect to TDS) was added, and the suspension was heated up to its boiling point. Concentrated HCl was then introduced dropwise through the condenser to the stirred mixture until all Zn reacted. The mixture was cooled and transferred into a separation funnel; the lower (acidic) phase was separated; and the hexane phase (forming a thick emulsion) was washed several times with a fresh, concentrated HCl to remove $ZnCl_2$, and then with water. To remove *p*-tolyl mercaptan (TM), into which TDS was converted by this reduction cleavage, the hexane phase was washed several times by an aqueous solution prepared by dissolving 2.4 g of NaOH and 2.4 g of NaCl in 20 mL of water (the presence of NaCl suppresses the formation of an emulsion) or by 3% (*w*/*v*) methanolic NaOH. Final washing was done with 20% (*w*/*v*) aqueous NaCl until neutral reaction of the aqueous phase was achieved. The hexane phase was then filtered through a paper filter, hexane was evaporated, and a slightly yellowish polymer was isolated (usual yield, 94 to 97% of theory).

Measurements

NMR

^{1}H-NMR spectra were recorded with a Bruker DPX-300 spectrometer at 300.1 MHz. 20% (*w*/*v*) solutions in $CDCl_3$ were measured at room temperature in 5-mm NMR tubes. Hexamethyldisiloxane, with a signal at 0.05 ppm from tetramethylsiloxane (TMS), was used as an internal standard; chemical shifts in the text and in the Figure 1 are referred to TMS. Measurements were performed with 90° pulses (32 scans), a spectral width of 5995 Hz, an acquisition time of 2.73 s, and a relaxation delay of 6 s.

Estimation of the Distribution of TDS and PB Between Two Conjugated Phases

Phase equilibria were approximated in a 250-mL glass, jacketed vessel, equipped with a capillary for sampling by a syringe. The liquids, forming the partially miscible solvent pair, and the solute [bis(*p*-tolyl)disulfide or the polymer] were introduced so that both conjugated phases had equal volumes and the overall concentration of the solute was about 0.1% (w/v). The system was heated up to some 55–60°C and then slowly cooled down and kept 1 h under occasional shaking at 25 $\pm$ 0.05°C before sampling.

Concentrations of bis(*p*-tolyl)disulfide (TDS) in conjugated phases of the partially miscible solvent systems of methanol–heptane, methanol–octane, and methanol–decane were determined spectrophotometrically (Hewlett-Packard 8451A diode array spectrometer; a quartz cell having the thickness of 0.1 cm; absorbances measured at 244 nm).

Concentrations of polymer in conjugated phases were determined gravimetrically after the evaporation of the solvents.

RESULTS AND DISCUSSION

Measuring the Degree of Hydrogenation and the Concentration of the Aromatic Contaminants/Substituents by ^{1}H-NMR

The degree of hydrogenation h of individual HPB or pHPB samples (or, alternatively, the mole fraction of residual unsaturated monomer units u, which is a quantity complementary to h) were determined by ^{1}H-NMR spectroscopy. The values of h are given in Tables I and II.

Spectroscopic data were treated by two alternative methods. As an illustration, the spectrum of the sample H-8 is shown in Figure 1.

In the first method, the signal of methyl protons must be separated from those of other aliphatic protons. To check if a systematic error was introduced by this separation procedure, the results thus obtained were compared with those supplied by the second method, as discussed below.

If the symbols I_{Me}, I_C, I_A, and I_B, denote, respectively, integrated intensities of bands of pro-

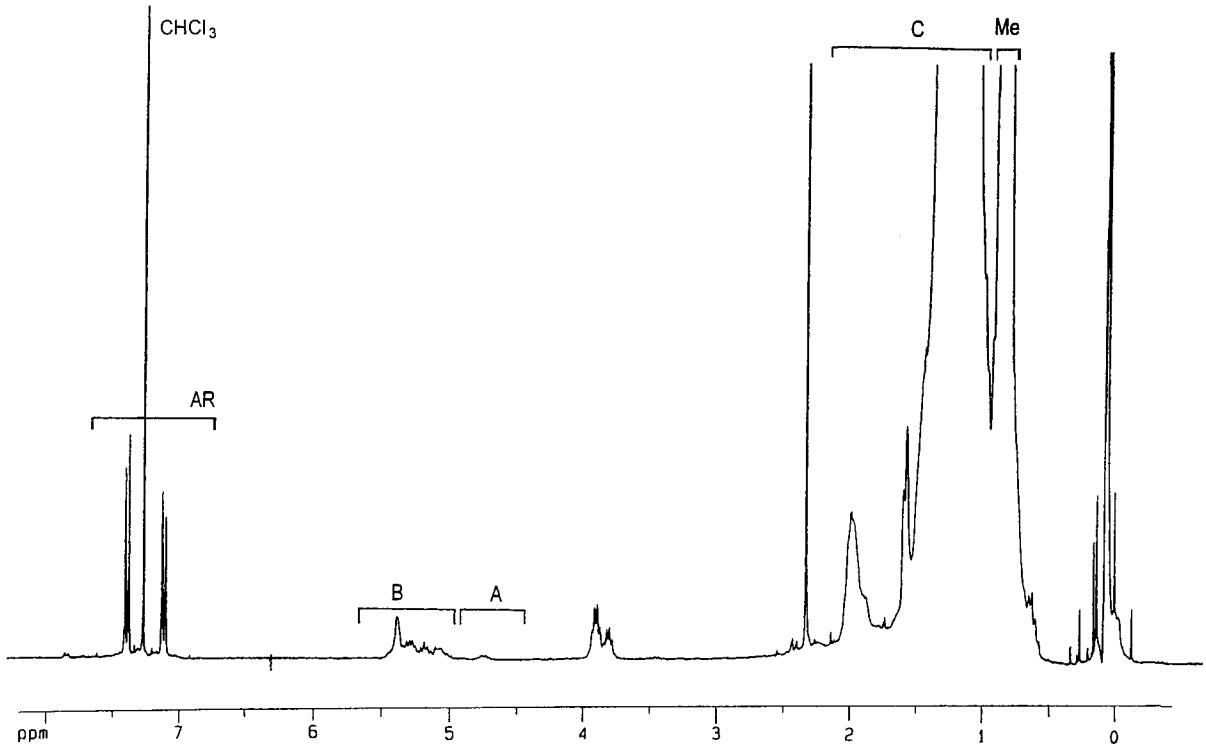


Figure 1 300.1-MHz ^{1}H-NMR spectrum of the sample H-8 in $CDCl_3$ at ambient temperature. A, B, C, AR, and Me denote those regions of the scale, where signals corresponding to olefinic A, olefinic B, aliphatic (except methyl), aromatic, and methyl protons appear, respectively (see the text).

Table II Characteristics of the Diimide Hydrogenation Products

			w_{AR} After Purification by					
			ME Only		ME + CHR		ME + Zn/HCl	
Run	[TSH]/[C═C]	h_{prod} (NMR)	NMR	EA	NMR	EA	NMR	EA
H-1[b]	2.00	0.999	17.3	16.9	13.3	7.9	—	—
H-2[a]	1.93	0.985	12.2	13.8	2.0	3.9	—	—
H-3[a]	1.99	0.994	19[c]		—	—	1.4	2.2
H-4[a]	2.00	0.999	21[c]		—	—	4.0	4.3
H-5[b]	4.96	0.996	5.5[c]		—	—	0.5	0.7
H-6[b]	4.98	0.998	6.6[c]		—	—	1.2	0.9
H-7[b]	3.01	0.995	3.1[c]		—	—	0.3	1.2
H-8[a]	4.41	0.983	2.2	2.6	0.6	<0.4	—	—
H-9[a]	6.23	0.992	6.5	7.2	0.3	<0.9	—	—

Hydrogenation performed [a]with or [b]without tri-*n*-propylamine.

[c] A gravimetric estimate calculated from the yield. [TSH]/[C═C] is a mole ratio of *p*-toluenesulfonylhydrazide and unsaturated monomer units of the polymer substrate in the initial reaction mixture, h_{prod} is the final degree of hydrogenation, w_{AR} is the mass fraction (in %) of aromatic moiety in the product, assuming it is free *p*-tolyl disulfide (TDS).

ME and CHR denote the isolation methods used (methanolic extraction and column chromatography).

Zn/HCl refers to the chemical method based on reduction cleavage of TDS.

EA stands for elemental analysis (% S).

tons in the regions of 0.75–0.80 ppm (methyl) and 1–2.3 ppm (aliphatic except methyl) and around 4.9 ppm and around 5.3 ppm (olefinic), then the degree of hydrogenation of 1,2 monomer units, $h_{1,2}$, and that of 1,4 monomer units, $h_{1,4}$ (mole fractions of saturated 1,2 and 1,4 units, related to all 1,2 and all 1,4 units, respectively), can be calculated according to eqs. (4a) and (4b), as follows.

$$h_{1,2} = (I_{Me}/3)/[(I_{Me}/3) + (I_A/2)] \quad (4a)$$

$$h_{1,4} = 2I_h/[2I_h + I_B - (I_A/2)] \quad (4b)$$

where

$$I_h = \{I_C - 2[I_B - (I_A/2)] - (5I_{Me}/3) - (3I_A/2)\}/8 \quad (4c)$$

For the total degree of saturation (mole fraction of all hydrogenated monomer units, related to all monomer units, irrespective of their isomerism) h, it holds that

$$h = x_{1,2}h_{1,2} + x_{1,4}h_{1,4} \quad (4d)$$

where $x_{1,2}$ and $x_{1,4}$ are mole fractions of 1,2 and 1,4 monomer units, determined from an independent ^{1}H-NMR measurement of the corresponding unsaturated precursor, having necessarily the same microstructure ($x_{1,2} + x_{1,4} = 1$).

To check the correctness of the separation of the peak of methyl protons, an alternative method was applied. If $I_{al} = I_{Me} + I_C$ stands for an integrated intensity of all aliphatic protons, then the degree of unsaturation of 1,2 units, $u_{1,2}$, and that of 1,4 units, $u_{1,4}$ (mole fractions of unsaturated 1,2 and 1,4 units, related to all units irrespective of their isomerism), were calculated using eqs. (5a) and (5b), as follows.

$$u_{1,2} = I_A/2I_u \quad (5a)$$

$$u_{1,4} = [I_B - (I_A/2)]/2I_u \quad (5b)$$

For I_u, we get

$$I_u = (I_{al}/8) + (3I_A/16) + (I_B/4) \quad (5c)$$

For the total degree of unsaturation (mole fraction of all unsaturated monomer units, related to all units, irrespective of their isomerism) u, it holds that

$$u = u_{1,2} + u_{1,4} \quad (5d)$$

and

$$u + h = 1 \quad (6)$$

These alternative methods of calculation yielded results that met the condition [eq. (6)] with deviations in the third or even fourth decimal place (therefore, only the values of h are given in Tables I and II). This means that the separation of the methyl band from other aliphatic bands was done satisfactorily.

Aromatic, sulfur-containing contaminants and/or substituents were also determined by ^{1}H-NMR (cf. Fig. 1). The form of the expression used for the calculation of the mole fraction of the contaminant or substituted monomer unit, x_{AR}, depends on the respective structures. To obtain x_{AR} for the cases in which the entity is free TDS or for the structure **C**, eq. (7a) was used; whereas for the cases in which the corresponding entity is the structure **A** or the structure **B** (cf. the introduction), eq. (7b) was applied.

$$x_{AR} = (I_{AR}/8)/[(I_{AR}/8) + (I_{Me}/3x_{1,2})] \quad (7a)$$

$$x_{AR} = (I_{AR}/4)/[(I_{AR}/4) + (I_{Me}/3x_{1,2})] \quad (7b)$$

Here, I_{AR} denotes the integrated intensity of the signals of the aromatic protons in the range of 6.9–7.7 ppm (except for the sharp peak at 7.24 ppm, which pertains to residual protons of $CDCl_3$ and was excluded from integration). The fraction $x_{1,2}$ is included as a correction (methyl groups are present on 1,2 units only).

The values of x_{AR} obtained for individual structures from ^{1}H-NMR spectra were transformed into the mass fractions w_{AR} and listed in Table III, in which a comparison with data from elemental analysis (% S) is also given. Discussion on the point is presented below.

Hydrogenations

Conditions of hydrogenations, that is, initial concentrations of individual reaction components, are given in Table I. Code numbers of the reaction runs are identical with those of the resulting samples of the hydrogenated polybutadienes (HPB) under study. In Table II, the results of partial characterization of the products, that is, the final degree of hydrogenation h_{prod}, the concentration

Table III Mass Fractions w_{AR} (%) of Aromatic, Sulfur-Containing Structures, Present in Diimide Hydrogenated Products

	From ^{1}H-NMR (Aromatic Protons)				From Elemental Analysis (% S)			
Sample	Free TDS	**A**	**B**	**C**	Free TDS	**A**	**B**	**C**
H-1	10.5	16.9	14.6	12.5	7.9	13.4	11.4	9.6
H-2	2.5	4.2	3.5	3.1	3.9	6.7	5.7	4.8
H-8	0.6	1.1	0.9	0.8	<0.4	0.7	0.6	0.5
H-9	0.3	0.5	0.4	0.4	<0.9	1.5	1.3	1.1

All values were determined after performing both purification steps (methanolic extraction and chromatography). They were calculated assuming that the structure is free bis(*p*-tolyl)disulfide (TDS), sulfon structure **A**, monosulfidic structure **B**, or bis-sulfidic structure **C** (see the introduction).

of contaminants w_{AR}, and, also, variation of these parameters with the preparation conditions are listed. When present, TPA was always used in an equimolar (or slightly higher) amount with respect to TSH.

Other characteristics of HPBs, like the concentration of OH end groups, are presented in a separate article.[11]

Three conclusions can be drawn from the data in Tables I and II.

First, as expected, the degree of hydrogenation increases with an increasing number of moles of TSH pertaining to one mole of (residual) C═C bonds of the substrate (ratio [TSH]/[C═C]), as follows from the comparison between H-1 and H-2, within the series H-5, H-6, and H-7, and between H-8 and H-9.

Second, with increasing [TSH]/[C═C], the concentration of free TDS remaining after the extraction step also increases (Table II).

Third, to get comparably high values of h (close to unity), [TSH]/[C═C] must be somewhat higher if pHPB is the substrate than if the runs start from PBs. However, as expected, the opposite is true when this mole ratio is converted by a simple calculation into the mass ratio of TSH to the starting polymer (the latter ratio is approximately an order of magnitude lower for the runs with pHPB). Although the decrease of consumption of TSH is not directly proportional to the decrease of the unsaturation of the substrate, it is still substantial.

Methods of Removing Free TDS

When TPA is present in the hydrogenation mixture (samples H-2 to H-4, H-8, and H-9), only small amounts of TSH fragments/derivatives add to the chain and, instead, the majority remains in the mixture in a free form as TDS. The problem therefore consists in finding conditions for removing free TDS from HPB without changing the structure of the polymer. Standard (re)precipitation techniques using solvent–precipitant systems are inapplicable for this low-molar-mass polymer under study because nonsedimenting milky emulsions are always formed.

It is obvious that the first purification step, that is, the extraction of the free contaminant (TDS) from the crude HPB product by the octane–methanol system, is insufficient (Table II). The reason is that the distribution of TDS between the conjugated phases is not very favorable. An attempt has therefore been made at finding a better system.

As a criterion, distribution coefficients k', determined for TDS and HPB in partially miscible solvent pairs consisting of an alkane (heptane, octane, and decane) and methanol, have been estimated (instead of the true Nernst distribution coefficients, k, which are defined for virtually immiscible liquids only) and listed in Table IV, from which the following conclusions are drawn.

1. For all alkanes used, the liquid–liquid extraction of TDS by methanol is unfavorable: the calculations show that diminishing the TDS concentration in the crude product below some 10% of the original value would require as many as 12 extraction cycles or more, provided that the volumes of both conjugated phases are equal.
2. Unfortunately, the undesirable transfer of certain portion of the HPB molecules from the alkane-rich to the methanol-rich phase increases in the same direction as the de-

Table IV Estimates of the Distribution Coefficient k' of bis(*p*-Tolyl)Disulfide (TDS) and Hydrogenated Polymer (HPB) in Conjugated Systems Alkane–Methanol at 25°C

	k'	
Alkane	TDS	HPB
Heptane	0.61	0.017
Octane	0.53	0.005
Decane	0.39	0.003

k' is defined as a ratio of mole concentration of the respective substance in the methanol-rich phase to that in the alkane-rich phase.

sirable extraction of TDS, that is, from decane to heptane. Although the loss of the polymer material caused by the methanolic extraction would seem negligible, there is a danger that polymer is fractionated according to its OH-functionality.

It can be concluded that the extraction of the alkane solutions by methanol can be used only for lowering the very high concentrations of TDS present in the crude polymer product (down to some 10 wt % at best) after the TSH hydrogenations. Such an extraction should be performed with a limited number of cycles only. We have chosen octane and five cycles as a compromise.

To further decrease the concentration of TDS in the bulk HPB (below the level of 1 wt %), we used the following two alternative methods.

1. Simple preparative column chromatography experiments were performed with partially purified HPB (pretreated by extraction) on activated silica. Heptane was used as the first eluent, washing out TDS and leaving HPB on the start. The latter component, which in the nonpolar solvent is firmly bound to the active sites of SiO_2 through the OH end groups, was then eluted by methyl-*tert*-butyl ether. In this way, both components were obtained in a fairly pure form, and the structure of the isolated low-molar-mass substance was confirmed by comparing its IR spectrum with that of authentic TDS. A qualitative chromatogram can be seen in Figure 2, from which it follows that, in addition to TDS, one more (smaller) peak of a nonpolymer component can be detected. An attempt at an identification by IR spectroscopy showed that this minority substance is an unspecified aliphatic hydrocarbon having its molecular chain longer than *n*-octane but shorter than HPB.
2. For the separation of large amounts of the HPB/TDS mixtures, however, the chromatographic method is impractical. For this case, we developed a chemical method, by which the TDS component was first converted into *p*-tolyl mercaptan (TM). This step is based on a reductive scission of the S—S bond of TDS by hydrogen released during the reaction of zinc and hydrochloric acid. Although the reaction proceeded in a three-phase system (unlike the standard procedure[13]), where the generation of hydrogen and the reductive scission itself took place in different phases, it was quite efficient. In the next step, TM was removed by washing the hexane solution of the HPB–TM mixture with aqueous NaOH because sodium mercaptid is water-soluble. In this way, it was possible to decrease substantially the concentration of TDS (cf. samples H-3 to H-7 in Table II). The chemical and chromatographic methods are roughly equally efficient.

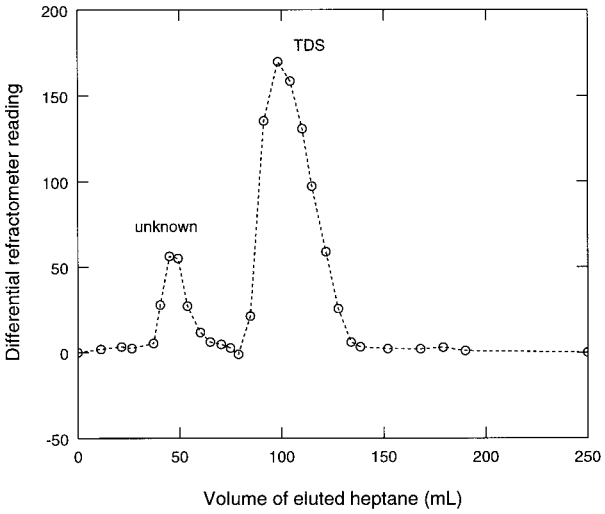


Figure 2 Chromatographic removal of the nonpolymeric components of the sample H-9 (ambient temperature; sorbent, activated silica; solvent, heptane). TDS is bis(*p*-tolyl) disulfide.

Attempts have also been made at performing other chemical modification of TDS in order to remove it from the mixture (disproportionation of the disulfide by sodium sulfide[13,14] and the reduction by sodium dithionite[13,15]), but these approaches failed, probably due to the fact that the reaction preceeded in two-phase systems.

Other possible approaches, such as reduction of the S—S bond by lithium aluminum hydride[13] and separation of HPB and TDS by ultrafiltration or molecular distillation of TDS, were omitted due to their inapplicability in larger scales.

Effect of Tri-*n*-Propylamine

It was reported[9] that TPA, which is a strong acceptor of protons, blocked the ionic addition of *p*-toluenesulfinic acid to the C═C bonds of the polymer substrate. This finding was confirmed also by our results: such an effect is most conspicuous if we compare the samples H-1 and H-2 (Table II), both of them prepared from totally unsaturated substrate (PB). If TPA was absent from the reaction mixture (H-1), the product contained a high level of an aromatic, sulfur-containing moiety, which could not be fully removed by chromatography. Most probably, this moiety is chemically bound to the polymer chain. For H-2, this level is, after the chromatographic separation, dramatically lower but still nonnegligible.

As expected, if pHPB is used as the hydrogenation substrate instead of PB, the presence of TPA is no more critical for the purity of the product, as follows from the comparison between, for example, H-5 and H-8: the former sample was prepared without, whereas the latter was prepared with TPA; and the concentrations of incorporated impurities (aromatic substituents) are comparable.

On the other hand, purity of the product is strongly affected by the fraction of unsaturated monomer units in the starting substrate, as follows for the comparison between H-2 and H-8: in both cases, TPA was present in the reaction mixture; but if totally unsaturated PB was used, the undesirable additions of TSH fragments or TSH derivatives were more probable than in the case of pHPB.

Nature of the Pendant Groups

We are convinced that the impurities remaining in the polymer products after the second purification step are, in fact, aromatic, sulfur-containing substituents on the polymer chain, which cannot be removed by physical methods. For the sake of simple comparison, the values of w_{AR} in the last four columns of Table II were calculated under a formal assumption that the impurity was free TDS in all cases. However, if such calculations were performed assuming that either sulfon or sulfide structures (**A**, **B**, or **C**; see the Introduction), bound directly to the chain, are present instead of free TDS, then, for the products purified by chromatography, only minor changes of w_{AR} were observed, being comparable, especially for H-8 and H-9, with the differences between the two measuring techniques used (NMR and elemental analysis), as illustrated by examples in Table III.

Obviously, using data in Table III, one cannot decide which of the structures **A**, **B**, or **C** predominates on the chain. However, from the preliminary results of thermooxidation of the HPBs, as measured by differential scanning calorimetry (DSC), it follows that our samples show exotherms, which should be absent if sulfon structures **A** are the only substituents present. If the sulfide structures are really attached to the chain, the exotherms should disappear or diminish after a gentle oxidation of the HPB by, for example, H_2O_2. These experiments, as well as DSC and Fourier transform infrared measurements, are the subject of a forthcoming article.[12]

This work was supported by the Grant Agency of the Academy of Sciences of the Czech Republic (grant number A4072902). The authors thank Drs. Jiří Hetflejš and Stanislav Šabata from the Institute of Chemical Process Fundamentals of the Academy of Sciences of the Czech Republic for performing the partial hydrogenations by Ziegler–Natta catalysts. Also acknowledged is the support from Kaučuk Group AS, Kralupy n. Vlt., Czech Republic.

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