

Structure of partially hydrogenated polybutadienes

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An analysis of the molecular structure of partially hydrogenated fractions of a monodisperse polybutadiene has been carried out in order to study the nature of the heterogeneous hydrogenation process. The polybutadiene was synthesized by polymerization of butadiene with *t*-butyl lithium in a non-polar medium. This reaction produces linear polybutadiene chains with about seven 1,2 addition units every 100 structural units. The catalytic hydrogenation of the polybutadiene fractions was done either in cyclohexane with Pd/CaCO₃ catalyst or in heptane with Pd/BaSO₄ catalyst. The reaction time was varied in order to obtain materials with different amount of unsaturations. The resulting polymers were characterized by gel permeation chromatography, differential scanning calorimetry, and infra-red spectroscopy. Solvent extraction using *n*-hexane was also performed over thin films of several samples of hydrogenated polybutadienes. The resulting fractions of the non-extracted material, and of some of the extracted ones, were analysed using infra-red spectroscopy. The results show that the hydrogenation reaction generates a bimodal distribution of polymer species for global conversions lower than approximately 89%. The catalytic reaction takes place in such a way that, in each adsorption step, approximately 89% of the unsaturated groups of each adsorbed molecule are hydrogenated. This process generates a mixture of polymers that are either highly hydrogenated poly(ethylene-1-butene-butadiene) copolymer or non-hydrogenated polybutadiene. The resulting blends are immiscible at all the studied global conversions (12–89%). © 1998 Published by Elsevier Science Ltd. All rights reserved.

(Keywords: polybutadiene; hydrogenated polybutadiene; blends)

Introduction

The ethylene-based polymer and copolymers constitute the most important family of polymeric materials today. They have endless commercial applications, and new resins are experiencing healthy growth. In this work we report the molecular characterization of a series of polymer blends obtained by partial hydrogenation of a monodisperse polybutadiene (PB) obtained by anionic polymerization¹. Partial hydrogenation of the PB reduces the number of the double bonds in the main chain and converts some of the 1-2 (vinyl) addition units into ethyl branches. The total hydrogenation of the PB yields a model copolymer of ethylene and 1-butene which highly resembles the structure of linear low density polyethylene^{2,3}. The rheology of these polymers in the melted state has been studied and will be reported elsewhere⁴.

Previous works have investigated the structure and morphological behavior of polybutadienes and totally hydrogenated polybutadienes of very narrow molecular weight distribution^{2–8}. Rosedale and Bates⁹ have analysed the mechanism of the catalytic hydrogenation of a polybutadiene. They studied the reaction of poly(vinylethylene) (PVE) in cyclohexane using palladium catalyst supported on calcium carbonate. It was found that this reaction initially proceeds by the hydrogenation of approximately 85% of the unsaturated units in individual PVE molecules during a single adsorption step. In the present article we analyse the structure of a series of partially hydrogenated polybutadienes (PHPB) which were obtained controlling the reaction time of the catalytic hydrogenation of an almost monodisperse polybutadiene with approximately 7% 1-2 addition¹.

Experimental

Materials. The nearly monodisperse PB used to obtain the copolymers was prepared by anionic polymerization of butadiene in cyclohexane using standard techniques^{1,10}. Both monomer (Instrument Purity, Matheson) and cyclohexane were purified, neutralized, and distilled in vacuum over sodium mirrors until they were free of moisture. The synthesis of the PB was done under vacuum at room temperature in a glass reactor using *t*-butyl lithium as initiator. The living polymer was terminated using anhydrous iso-propyl alcohol. A small amount of 0.01 wt% of Santonox (Monsanto) in methanol was added before precipitation to prevent the oxidation of the PB. Finally, the polymer was dried in vacuum and then stored at low temperature. The use of cyclohexane as solvent in the polymerization process produces a PB with a small amount of vinyl groups¹. The relative amount of unsaturations determined by infra-red (i.r.) (see below) on the PB yields 7.3, 47.3 and 45.4% of 1,2-vinyl, 1,4-*trans* and 1,4-*cis* double bonds, respectively.

Hydrogenation. The partial hydrogenation of the PB was performed in a 2 l Parr reactor working at 3.55×10^6 Pa of hydrogen pressure. Seven different materials were obtained by controlling the reaction time. The partially hydrogenated materials are identified with the name PHPB#, where # corresponds to the average degree of hydrogenation calculated from Fourier transform i.r. (FTi.r.) results. The PHPB02, PHPB12, PHPB21 and PHPB57 materials were obtained in 0.5 wt% solution in cyclohexane at 75°C with 0.50 g of Pd/CaCO₃ catalyst (Strem) per g polymer in reactions that lasted from approximately 0.5 to 1 h. The PHPB38, PHPB89 and PHPB100 materials were obtained in 0.5 wt% solution in heptane at 98°C with

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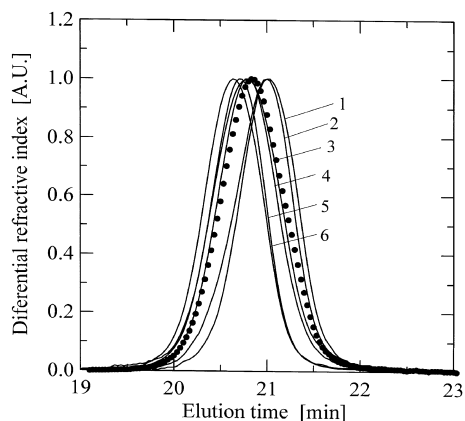


Figure 1 Chromatograms of the PB and the partially hydrogenated samples of the same PB. (1) PB; (2) PHPB12; (3) PHPB38; (4) PHPB57; (5) PHPB89; (6) PHPB100; ●, curve calculated by adding curves 1 and 5 previously normalized to equal areas to form a blend with a 50/50 composition

0.40 g of Pd/BaSO₄ catalyst (Strem) per g polymer. These reactions were allowed to proceed from approximately 1 to 12 h. The totally hydrogenated polybutadiene, PHPB100, is a model copolymer of ethylene and 1-butene which resembles the linear low density polyethylene. More details of the procedures followed during the polymerization and the hydrogenation may be found elsewhere².

Structure characterization. The number- and weight-average molecular weights (M_n and M_w) of the PB were obtained by gel permeation chromatography (g.p.c., Waters) at room temperature using μ -Styragel columns (Styragel) of 10⁵, 10⁴, 10³ and 500 Å. Standard calibration procedure was followed using monodisperse PS samples with toluene as solvent carrier and published values of the Mark-Houwink parameters¹¹. Chromatograms of the hydrogenated materials and of the PB were obtained at 140°C in a Waters 150-C ALP/GPC instrument using 1,2,4 TCB as the solvent and PLGel columns (Polymer Labs) of 10⁶, 10⁴ and 500 Å. The calibration was performed using monodisperse PS samples. The molecular weight of the totally hydrogenated PB was calculated by standard calibration with monodisperse PS samples and using Mark-Houwink coefficients for PS¹² and linear polyethylene¹³ in TCB.

The amount and type of unsaturations in the PB were studied by i.r. spectroscopy (FTi.r., Nicolet 520) using solutions of approximately 1.5% (wt/v) in carbon disulfide. The relative amount of 1,2-vinyl, 1,4-*trans* and 1,4-*cis* unsaturations were determined from the i.r. absorption bands at 910, 966 and 735 cm⁻¹ using molar absorptivities of 173.5, 141 and 25.3 l mol⁻¹ cm⁻¹ respectively¹⁴. No information about the distribution of the different types of unsaturations may be obtained from this technique. The global degree of hydrogenation of the PHPB materials was established by measuring the concentration of the remaining 1,4-*trans* and 1,2-vinyl double bonds by FTi.r. spectroscopy and calculating the ratios with respect to the amount of the equivalent unsaturations in the original PB. The study was done preparing solutions of approximately 2% (wt/v) in toluene at 90°C. The absorption band corresponding to the 1,4-*cis* unsaturations was not measured because it overlaps with that of the -CH₂- groups and some of the toluene bands.

A thermal analysis of all the materials was performed in a

Perkin Elmer DSC-2C instrument. A heating rate of 10°C min⁻¹ was used for all the polymers both in the runs from -140 to 0°C and from -10 to 120°C. In this last set of runs, the same initial history of melting at 120°C and cooling to -10°C at a rate of 20°C min⁻¹ was imposed to all the samples before performing the experiments.

Four of the partially hydrogenated PB were exposed to an extraction process with *n*-hexane. This solvent was selected because the PB is soluble in hexane while the highly hydrogenated PB is not. Small samples of PHPB12, PHPB38, PHPB57 and PHPB89 were immersed in approximately 300 ml of *n*-hexane at ambient temperature in the presence of Santonox for periods of more than 7 days. This procedure was repeated a second time to assure the complete extraction of soluble material before the samples were dried in vacuum. The fractions of non-extracted polymer of each sample were dried and weighted to determine the proportion of extracted material. Films made of these undissolved polymers were analysed by FTi.r. spectroscopy to measure the concentration of the remaining 1,4-*trans* and 1,2-vinyl double bonds. The extracted portion of one of the materials, the PHPB38, was precipitated in cold methanol, dried and then dissolved in carbon disulfide to be analysed by FTi.r. to confirm the results obtained from the analysis of the undissolved polymers.

Results and discussion

Molecular weights and distribution. The number- and weight-average molecular weight of the PB were determined to be 70 600 and 75 000 g mol⁻¹ respectively. The ratio M_w/M_n , which is a measure of the polydispersity (PD) of the system, has a value of 1.06. The characterization of the PHPB100 yields number- and weight-average molecular weights of 74 000 and 77 300 g mol⁻¹ respectively with a PD of 1.045. The number- and weight-average molecular weights of the PHPB100 calculated from the PB precursor are $M_{\text{PHPB100}} = 56 \times M_{\text{PB}}/54$ which gives $M_n = 73 200$ g mol⁻¹ and $M_w = 77 800$ g mol⁻¹. These values are in excellent agreement with the results from the g.p.c. measurements.

Figure 1 shows the chromatograms of the original PB, the PHPB100 and four of the partially hydrogenated materials, all of them obtained at 140°C in TCB. All the chromatograms have been normalized with the maximum of the corresponding curve for an easier comparison of the results. The chromatograms show a gradual shift to smaller elution times as the saturation level increases. The polybutadiene exhibits the longest elution time which corresponds to more flexible molecules with smaller hydrodynamic volume. The corresponding hydrogenated molecule of the PHPB100 is less flexible and has a larger hydrodynamic volume. This is in accordance with the unperturbed mean-square end-to-end distance $\langle R^2 \rangle_0/M$ values reported at 140°C by Fetters *et al.*⁷ for a polybutadiene with 10% of 1,2-vinyl groups ($\langle R^2 \rangle_0/M = 0.876 \text{ \AA}^2 \text{ g}^{-1} \text{ mol}$) and a hydrogenated polybutadiene with 2% of ethyl branches per 100 skeletal carbons ($\langle R^2 \rangle_0/M = 1.21 \text{ \AA}^2 \text{ g}^{-1} \text{ mol}$). The chromatograms measured by Rosedale and Bates for PVE (100% vinyl content) and samples of partially hydrogenated PVE and totally hydrogenated PVE (PEE) exhibit the opposite effect. In this case the time of elution of the PVE was the smallest. This is also in agreement with the values of $\langle R^2 \rangle_0/M$ reported for PVE ($\langle R^2 \rangle_0/M = 0.664 \text{ \AA}^2 \text{ g}^{-1} \text{ mol}$) and PEE ($\langle R^2 \rangle_0/M = 0.485 \text{ \AA}^2 \text{ g}^{-1} \text{ mol}$) by Fetters *et al.*⁷. The PEE is a molecule with a smaller hydrodynamic volume than the original PVE.

Table 1 Results of FTi.r. spectroscopy and thermal analysis. The FTi.r. measurements on PB yield: 47.3, 45.4 and 7.3% of 1,4-*trans*, 1,4-*cis* and 1,2-vinyl double bonds respectively

Material	I.r. measurements (% of hydrogenation)			Thermal analysis	
	1,4- <i>trans</i> ^a	1,2-vinyl ^a	global% ^b	T _g (°C)	T _m (°C)
PB	0	0	0	- 97	-
PHPB02	2	2	2	- 97	104
PHPB12	12	9	12	- 96	104
PHPB21	21	26	21	- 95	101
PHPB38	38	31	38	- 98	103
PHPB57	57	63	57	- 97	104
PHPB89	88	> 99.5	89	-	103
PHPB100	> 99.5	> 99.5	> 99.5	-	106

^a Amount of 1,4-*trans* and 1,2-addition units that have been saturated during the process of hydrogenation, relative to the equivalent unsaturations existing in the PB

^b Global degree of hydrogenation in the material calculated as: $\text{global\%} = 0.07 \times \% \text{ of saturated 1,2-units} + 0.93 \times \% \text{ of saturated 1,4-}i\text{trans}$

Table 2 FTi.r. results corresponding to the undissolved portions of some of the partially hydrogenated polybutadienes

Material	I.r. measurements (% of hydrogenation)			wt% ^c	global% ^d
	1,4- <i>trans</i> ^a	1,2-vinyl ^a	average% ^b		
PHPB12	89	96	89	11	10
PHPB38	92	96	92	41	38
PHPB57	84	96	85	63	53
PHPB89	90	> 99.5	91	98	89

^a Amount of 1,4-*trans* and 1,2-units that have been saturated, relative to the equivalent unsaturations in the PB

^b Average degree of hydrogenation of the undissolved sample calculated as: $\text{average\%} = 0.07 \times \% \text{ of saturated 1,2-units} + 0.93 \times \% \text{ of saturated 1,4-}i\text{trans}$

^c Weight of the undissolved material relative to the weight of the analysed sample

^d Global degree of hydrogenation of the PHPB calculated as: $\text{global\%} = \text{weight\%} \times \text{average\%/100}$

The chromatograms plotted in *Figure 1* show a slight increase in the width of the curves at intermediate concentrations. Curves 3 and 4 begin very near curves 5 and 6 at small elution times, while they are near curve 1 and 2 at larger elution times. These chromatograms do not show the bimodal distribution seen by Rosedale and Bates, probably because there is a smaller difference in the hydrodynamic volume of the molecules considered in our study. *Figure 1* includes the curve (full dots) obtained by adding the chromatograms of PB and PHPB89 equally weighted and previously normalized to equal areas. This curve, which corresponds to the expected result for the ideal blend of PB and the highly hydrogenated PB, shows no evidence of a bimodal distribution.

Chemical microstructure. *Table 1* shows the amount of 1,2-vinyl and 1,4-*trans* unsaturations in each material calculated by FTi.r. relative to the equivalent unsaturations in the PB which has 7.3, 47.3 and 45.4% of 1,2-vinyl, 1,4-*trans* and 1,4-*cis* double bonds respectively. Due to the small amount of 1,2-vinyl double bonds, the absorbance of the corresponding peak was more difficult to measure than that of the 1,4-*trans* unsaturations. Errors of approximately 2 and 30% were calculated in the data of the percentage of hydrogenation of the 1,4-*trans* and 1,2-vinyl double bonds respectively. The average degree of hydrogenation of each PHPB was calculated weighing the results for the 1,4-*trans* and 1,2-vinyl unsaturations with factors of 0.93 and 0.07 respectively, which reduces the effect that may cause the larger error in these last measurements. The procedure that we have followed assumes that the -*cis* and -*trans* double bonds are hydrogenated in the same proportion, and that

they represent 93% of the total number of double bonds in the original PB. This technique yields global results of the state of hydrogenation of the polymers but gives no information of the distribution of the hydrogenated unsaturations in the molecules. Using ¹H nuclear magnetic resonance (n.m.r.) and ¹³C n.m.r., Carella *et al.*³ were able to conclude that the vinyl and ethyl groups in PB and totally hydrogenated PB with low vinyl content are essentially random.

After the extraction with *n*-hexane, it was found that part of the samples remained undissolved. This portions were dried and weighted. *Table 2* shows the resulting wt% of non-extracted material for each PHPB analysed. The precipitated and dried extracted portion of the soluble part of the PHPB38 was analysed by FTi.r. showing the same proportions of unsaturated double bonds than the original PB, i.e. this part of the PHPB38 was not hydrogenated during the hydrogenation process. *Table 2* also presents the results from FTi.r. spectroscopy performed on the insoluble part of each sample. The degree of hydrogenation calculated for the four cases, which are shown in the fourth column of the table, are very similar and do not show a special dependency with the global degree of hydrogenation. The average result for the four analysed samples gives 89% of saturated double bonds. The last column in *Table 2* lists the global degree of hydrogenation of each material calculated considering the PHPB as a blend of a highly hydrogenated PB (with the average degree of hydrogenation given in the third column of the table) and non-hydrogenated PB. These results are almost equal to the global degree of hydrogenation measured for the whole materials (see *Table 1*).

These results are consistent with the hypothesis that the hydrogenation process of PB, both in cyclohexane and in

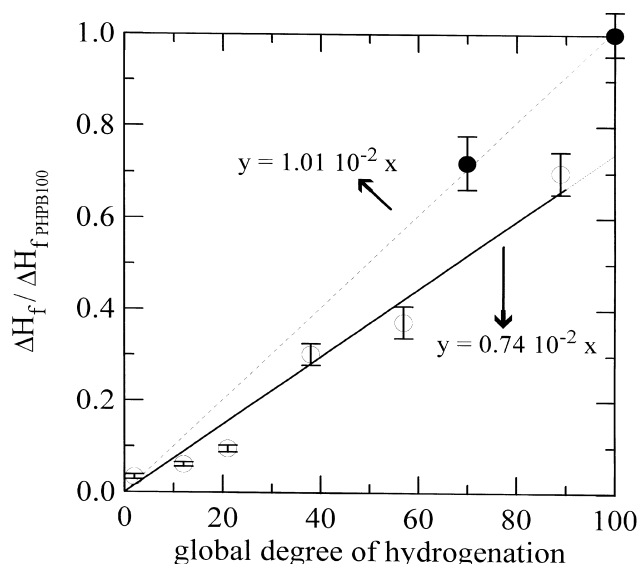


Figure 2 Heat of fusion of the hydrogenated polymers relative to that of the PHPB100 material plotted as a function of the global degree of hydrogenation. ○, hydrogenated polymers, ●, prepared 70/30 blend of PHPB100 and PB. Full line, linear fit of the data for conversion less than 89%. Dashed line, linear fit of the data for the prepared blend and the PHPB100 material

heptane, proceeds in such a way that each polymer molecule is hydrogenated about 89% during a single adsorption step for all conversions smaller than 89%. A similar conclusion was obtained by Rosedale and Bates⁹ for the catalytic hydrogenation of PVE in cyclohexane using palladium catalyst supported on calcium carbonate. Using size-exclusion chromatography and ¹H n.m.r. spectroscopy, these authors found that this process initially proceeds by the hydrogenation of approximately 85% of the repeat units in individual PVE molecules during a single adsorption step from solution. The approximate concentration of 85% was concluded from ¹H n.m.r. results for the extracted polymer of only one partially hydrogenated PVE which had 47% of all available vinyl repeat units hydrogenated. They qualitatively explained this behaviour by using the adsorption energies reported for saturated and unsaturated simple hydrocarbon molecules on group VIIIA metals. Rosedale and Bates concluded that initially the unsaturated polymer molecules easily adsorb on palladium crystallites because of the highly favourable interaction energy. As the hydrogenation takes place the affinity of the polymer with the surface reduces but the molecules are sufficiently dynamic to allow conformational rearrangements that expose new unreacted parts of the chain to the surface of the catalyst prolonging the adsorption and increasing the degree of hydrogenation.

Physical properties. The results of the differential scanning calorimetry (d.s.c.) measurements are also listed in Table 1. A glass transition temperature (T_g) of -97°C was measured for the PB which agrees with the expected value of the T_g of a polybutadiene of this microstructure³. A T_g was measured for all the PHPB tested in the interval from -140 to 0°C . The obtained results show no dependence of the detected T_g with the state of hydrogenation of the polymers. The resulting average T_g for the five PHPB analysed has a value of -96.6°C (with standard deviation of 1.1°C) which is also the T_g of the PB. No transition was detected for the PHPB100 in this range of temperature.

In the range from -10 to 120°C , all the hydrogenated materials go through an endothermic process corresponding

to a melting point. All the partially hydrogenated PB present a very similar melting temperature (average $T_m = 103.2^\circ\text{C}$ with standard deviation of 1.2°C). Only the PHPB100 shows a slightly higher melting point ($T_m = 106^\circ\text{C}$). Figure 2 shows the value of the heat of fusion of each PHPB relative to that of the PHPB100. These data suggest a linear increase of the heat of fusion with the increase of the global degree of hydrogenation up to a conversion of at least 89%. The full line in Figure 2 corresponds to the linear fit of the data for global conversions lower than 89%. The extrapolation to 100% conversion (dotted line) is a value much lower than the heat of fusion of the totally hydrogenated PB. This is a consequence of the difference in crystalline structure of the PHPB89 and the PHPB100 materials due to the presence of non-hydrogenated portions in the PHPB89 molecules. To test this conclusion a blend of 70% PHPB100 and 30% PB was prepared and analyzed in the d.s.c. The value of the heat of fusion measured for this blend, which is also shown in Figure 2, falls over a line of slope 1, that passes through the origin and does not follow the behaviour of the partially hydrogenated blends.

The above results show that the blends of PB and PHPB89 obtained by partial hydrogenation of the PB for small and intermediate conversions (12–89%) are immiscible blends. This conclusion was corroborated with rheological results⁴, which show that all the PHPB have the same melting temperature of approximately 110°C , above which they behave as a melt, even in the case of the PHPB02.

Conclusions

The catalytic hydrogenation of the PB with a low level of 1,2 addition initially proceeds by hydrogenating approximately 89% of the unsaturated units in individual polymer molecules during a single adsorption step from solution. In consequence, the polymer resulting from the hydrogenation process has a bimodal distribution consisting of unreacted PB and approximately 89% hydrogenated PB. Given more time and the sufficient amount of catalyst, the hydrogenation continues up to complete saturation. There was found to be no dependence in the results of the characterization with the solvent (cyclohexane or heptane) or the catalyst (Pd/CaCO₃ or Pd/BaSO₄) used in the hydrogenation process. The blends obtained for global conversions lower than approximately 89% are immiscible. The glass transition and melting temperatures measured for these materials show no dependency with the composition of the blend, and the heat of fusion increases linearly with the degree of hydrogenation from 0 to 89% conversion. The 89% saturated PB has only a trace of non-reacted PB and further reaction produces a change in molecular structure which is the cause of the slight shift in melting temperature and the higher heat of fusion measured for the PHPB100 material.

Acknowledgements

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