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Spectroscopic Studies of an Ambient-Pressure Process for the Selective Hydrogenation of Polybutadienes

H. G. M. Edwards,[*,†] **D. W. Farwell,**[†] **A. F. Johnson,**[†] **I. R. Lewis,**[†] **N. J. Ward,**[†] **and N. Webb**[‡]

Chemistry and Chemical Technology, Interdisciplinary Research Centre in Polymer Science and Technology, University of Bradford, Bradford, West Yorkshire, BD7 1DP England, and Castrol Research Laboratories, Whitchurch Hill, Pangbourne, Reading, Berkshire, RG8 7QR England

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ABSTRACT: The effectiveness of a low-pressure hydrogenation process for the selective hydrogenation of the vinyl-1,2, cis-1,4, and trans-1,4, structural units in high molecular weight polybutadienes has been explored using ^{1}H NMR, FT-IR, and Raman spectroscopy. The spectroscopic results indicate that it is possible to monitor the hydrogenation process by analysis of partially hydrogenated polybutadienes. The NMR measurements have made it possible to see the incorporation of an aromatic impurity in the polymer which results from a side reaction during hydrogenation. The first report is made of the use of Raman spectroscopy for analyzing the hydrogenation of a polydiene, and it is shown that FT-IR represents an improvement on earlier dispersive measurements of these processes.

Introduction

The polymerization of 1,3-butadiene usually gives rise to products which have a mixture of 1,4 and 1,2 structural units. The 1,4-addition product comprises a cis or trans isomer, and the 1,2-adducts might be isotactic, syndiotactic, or atactic, or some mixture of these structural types (Figure 1).

The determination of the microstructure of polybutadienes by Raman spectroscopy is a relatively simple procedure[1,2] and provides more accurate results[3] than that from infrared determination.[4,5] Cornell and Koenig[1] reported the first Raman spectroscopic study of polybutadienes in which the microstructure was determined quantitatively from the ν(C=C) Raman bands of vinyl, cis-1,4, and trans-1,4 units at 1640, 1650, and 1664 cm^{-1}, respectively, from peak height determinations. This method suffered from the incomplete resolution of the ν(C=C) Raman bands arising from the three microstructures, especially when one or more species is in low concentration. Computer-based curve-resolution packages now make the quantitative resolution of overlapping spectral peaks a relatively simple task.

Polybutadienes are partially hydrogenated in order to enhance their oxidative stability and thus increase their range of applications. Many hydrogenation methods have been used; some require harsh conditions, e.g., high temperature and/or high pressure, others are expensive.[6,7] A mild method of hydrogenation[8,9] which relies on ambient-pressure conditions has been described and forms the basis of the work described here. This method relies on the chemical decomposition of a reactive precursor. In this work, a diimide species was generated from *p*-toluenesulfonyl hydrazide by the following reaction.

$$CH_3C_6H_4SO_2NHNH_2 \rightarrow CH_3C_6H_4SO_2H + NH{=}NH$$

It has been suggested[8] that an impurity may be incorporated during the hydrogenation process

$$CH_3C_6H_4SO_2H + H_2C{=}CHCHRR' \rightarrow CH_3C_6H_4SO_2CH_2CH_2CHRR'$$

where, for polybutadiene, R and R′ = CH_2.

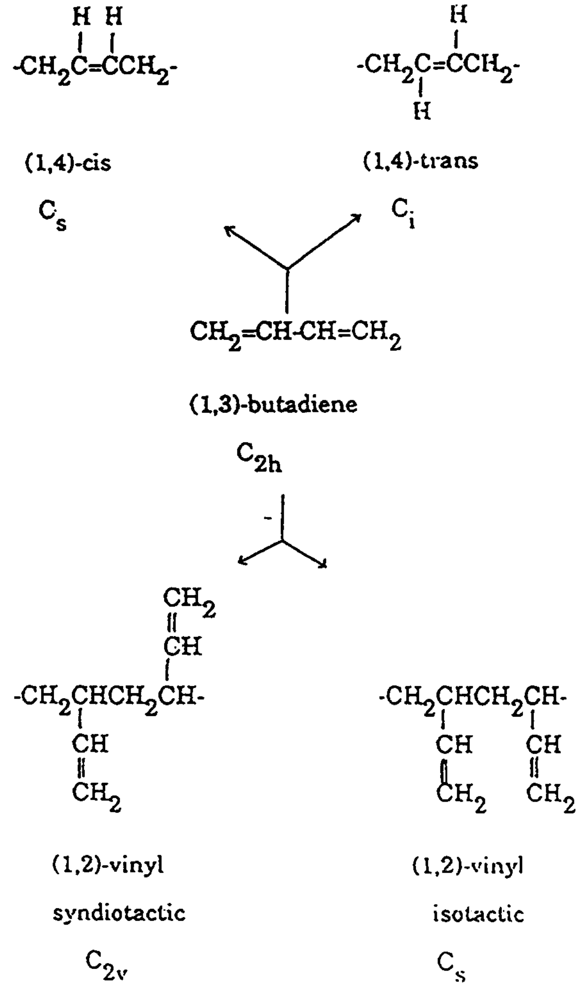

Figure 1. Polymerization routes for 1,3-butadiene together with local molecular symmetry point groups.

Experimental Section

Hydrogenation. Polybutadiene (Aldrich 18,128-2; 1.50 g) was dissolved in hot dry xylene (80 mL) with continuous stirring under a nitrogen atmosphere. Then *p*-toluenesulfonyl hydrazide (10.43 g) in dry xylene (70 mL) was added and the temperature raised to 115 °C. After 2 h the reaction was complete and solid *p*-toluenesulfonyl residues were removed by filtration from the

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[†] University of Bradford.

[‡] Castrol Research Laboratories.

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hot solution. The filtrate was added to an excess of methanol (500 mL) and the polymer precipitated out as a white solid. This was recovered by filtration and dried in a vacuum oven (740 mmHg, 40 °C) for 24 h.

The hydrogenation was repeated for different initial weight/weight ratios of catalyst to polybutadiene, for different total hydrogenation times, with several solvents, and with polymers of different microstructural compositions (i.e., different cis-1,4, trans-1,4, and vinyl compositions). The homopolybutadienes were synthesized in our laboratories. All were of high molecular weight (>150 000), and each had a different microstructural composition. The polymer syntheses have been described in detail elsewhere.[2] The materials were prepared by well-established high-vacuum techniques[2] using *sec*-butyllithium (Aldrich) as initiator to ensure rapid initiation rates in the hydrocarbon solvent used. Both the 1,3-butadiene monomer (Aldrich) and cyclohexane (Aldrich; HPLC grade) were purged with *n*-butyllithium and distilled in vacuo before use.

Analysis of Hydrogenated Polymer. 1. Determination of Residual Unsaturation by Iodination. Accurately weighed samples of the hydrogenated polymer (0.5 g approximately) were dissolved in boiling xylene (100 mL). The solution was cooled and mixed with a 20% solution of trichloroacetic acid in carbon tetrachloride. An excess of iodine in carbon tetrachloride was added, and this was followed by mercury(II) acetate solution (25 mL; 30 g/L of glacial acetic acid). The mixture was allowed to react in the dark for 2 h. Then the solution was shaken with a potassium iodide solution (7.5%; 75 mL) and the excess iodine was titrated with sodium thiosulfate (1 M) using starch as an indicator. The unsaturation units in the polymer were calculated from the amount of iodine consumed.

2. Infrared Spectroscopy. Infrared spectra were obtained with a Perkin-Elmer Model 1720-X Fourier transform infrared spectrometer fitted with a mercury cadmium telluride (MCT) detector operating at 77 K. Polybutadiene films were cast from a 2% solution in carbon tetrachloride onto a sodium chloride window, and the spectra were recorded using air as a background. Spectra were recorded at 0.5-cm^{-1} resolution over the range 4000–550 cm^{-1} using an accumulation of 10 scans. Data were collected in the spectrometer data station and transferred onto an IBM-compatible personal computer for subsequent data analysis (Figures 2 and 3).

3. Raman Spectroscopy. Raman spectroscopic studies were undertaken on the solid polybutadiene samples mounted on a glass window 60° to the plane of the laser beam. Excitation was effected using a Spectra-Physics Model 2020/5 argon ion laser operating at 488 nm with a nominal output of 1.5 W at 488 nm. The scattered radiation was analyzed using a SPEX Industries Model 1401 spectrometer with a reciprocal linear dispersion of 20 cm^{-1} mm^{-1} at 488.0 nm and photon-counting detection using an EMI 9789 QA photomultiplier.

Acquisition of data and control of the spectrometer was accomplished using a Nicolet 1180 microcomputer. A standard curve resolution program on the Nicolet 1180 microcomputer enabled the resolution of the ν(C=C) bands, of vinyl, cis-1,4, and trans-1,4 units at 1640, 1650, and 1664 cm^{-1}, respectively, to be achieved and band areas determined (Figure 4). Calibration was effected using a neon emission spectrum, and wavenumbers are correct to within 1 cm^{-1}.

The linearity of response of the spectroscopic instrumentation used in the microstructure determination had previously been verified,[10] using systems of known internal-field effects, and a geometric-optical[11] efffect of 1 was determined. Quantitative determination of the unsaturation in the polybutadiene samples was possible as the measured band areas were directly proportional to species concentration. As the ν(C=C) types are all Raman active, then the ratio of the measured band of microstructure x, $[A^x]$, to the total area of the band envelope, $[A^{tot}]$, represents the percentage composition of the species in the polybutadiene sample.

$$\%\ \text{species of microstructure}\ x = 100[A^x]/[A^{tot}]$$

4. ^{1}H NMR Spectroscopy. Polymers were analyzed with a JEOL JNMR GX 270-MHz Fourier transform nuclear magnetic resonance spectrometer using a 2% solution in chloroform in all cases. Proton spectra were acquired using 64 scans from δ −1 to +10 and the chemical shift scale optimized to show the aromatic region.

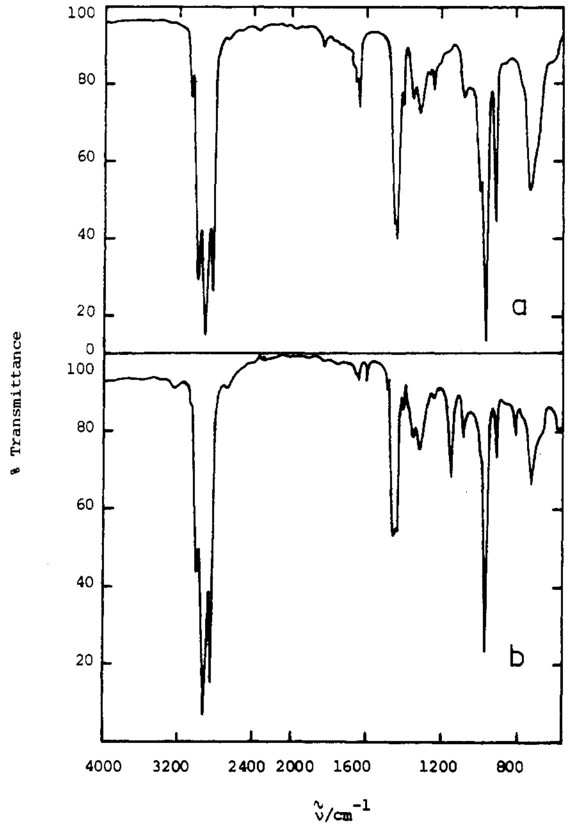

Figure 2. Infrared spectra of two polybutadienes of different microstructures in the region 4000–550 cm^{-1}.

Results

The FT-IR and Raman spectra showed features not expected for the hydrogenated polybutadiene, and these are presented in Table I. A Raman spectroscopic study of the polymers produced in the hydrogenation reaction had not been previously reported. The observed bands in the IR and Raman spectra have been assigned on the basis of IR[12] and Raman[13] studies of model compounds such as *p*-xylene, *p*-toluenesulfonic acid, and diphenyl sulfoxide.

The microstructure, after hydrogenation, was recorded, and the results are given in Table II along with the residual unsaturation for a single polymer prepared under different, polymer to diimide concentration, hydrogenation conditions. The Raman spectra over the 1550–1750-cm^{-1} region, for the samples in Table II which have different degrees of hydrogenation, are shown in Figure 5.

The NMR evidence for aromatic incorporation can be seen in Figure 6, and assignments are made from the NMR[14] studies of model compounds, namely, *p*-xylene, *p*-toluenesulfonic acid, and diphenyl sulfoxide.

Discussion

The NMR spectra of the nonhydrogenated and hydrogenated polymer present evidence of the incorporation of an aromatic impurity. The hydrogenated polymer shows two peaks in this region, centered on 7.35 and 7.78 ppm. The coupling constants, J = 7.51 and 6.96 Hz, in this region, provide evidence of a para-disubstituted benzene ring, which is in agreement with the mechanism of impurity incorporation suggested in this work.

The infrared spectrum shows absorptions between 3000 and 3100 cm^{-1} which have been ascribed to the aromatic

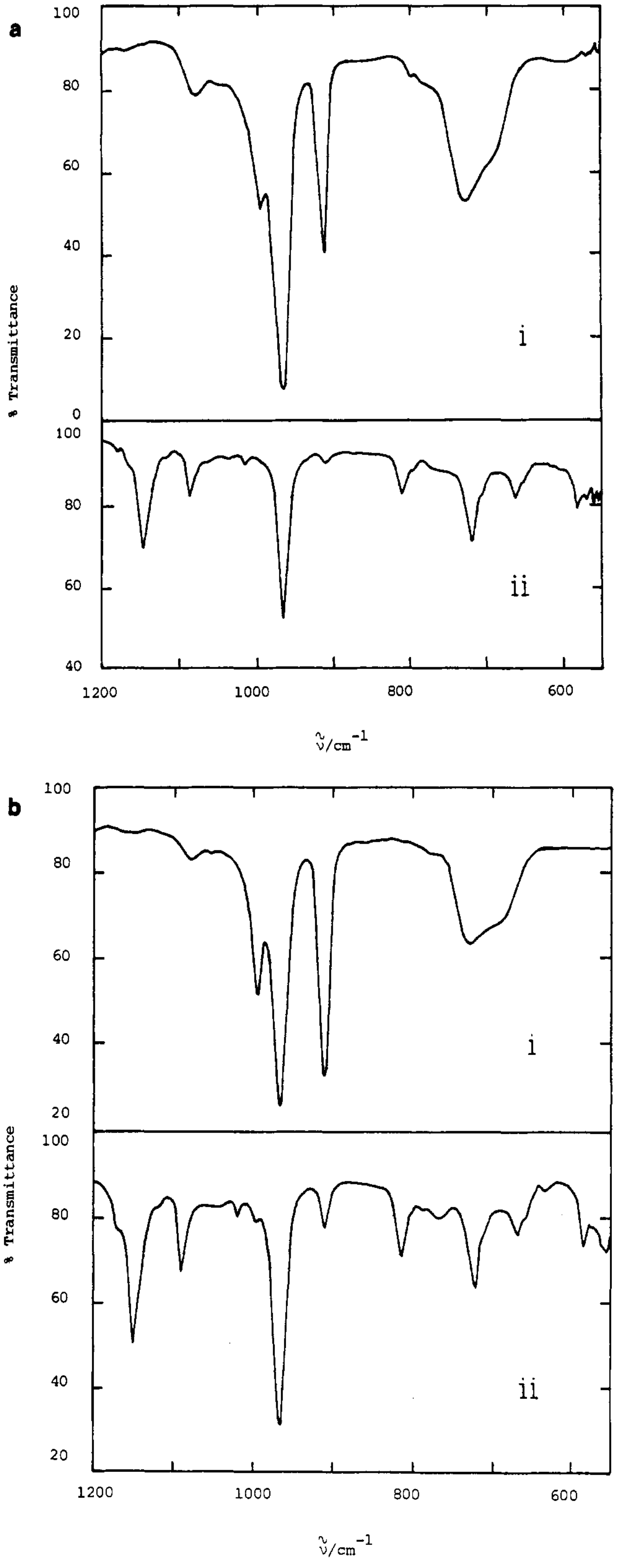

Figure 3. (a) Infrared spectra of polybutadiene (Aldrich) before (i) and after (ii) hydrogenation in the region 1200–550 cm^{-1}. (b) Infrared spectra of an anionically prepared polybutadiene before (i) and after (ii) hydrogenation in the range 1200–550 cm^{-1}.

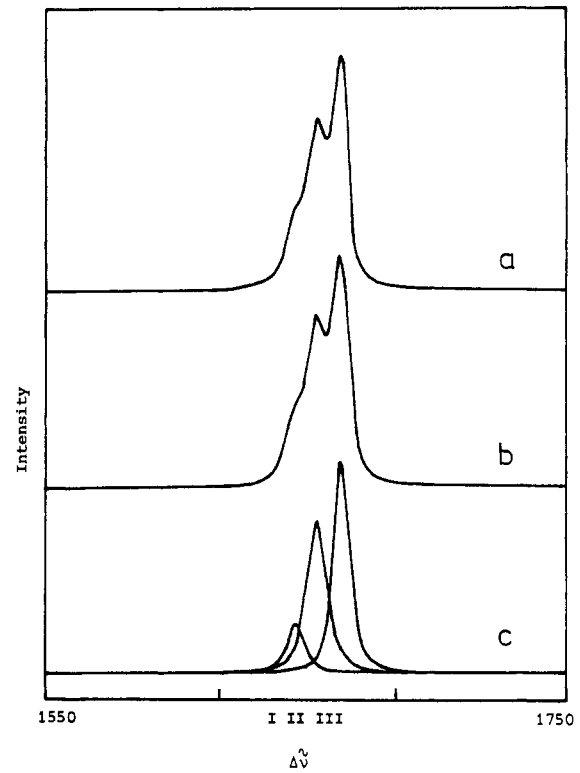

Figure 4. Raman spectra of polybutadiene (Aldrich) in the region $\Delta\nu$ = 1550–1750 cm^{-1}: (a) observed spectrum, (b) calculated spectrum, (c) resolved spectrum obtained from CAP for (I) vinyl, (II) cis-1,4, and (III) trans-1,4.

Table I
Vibrational Wavenumbers and Assignments of the Impurity Incorporated during the Hydrogenation

approximate description of band assignments	wavenumber observed, cm^{-1}	
	infrared	Raman
ν(CH)	3075	3062
ν(CC) aromatic	1597	1600
ring stretching	1576	1580
	1490	1500
	1436	1450
		1000
ν_a((C–)SO$_2$(–C))	1314	1331
ν_s((C–)SO$_2$(–C))	1147	1152
δ(C–H) in plane	1088	1090
$\nu_{(s)}$((C–)SO$_2$(–C))	1060	1040
ρ(C–H) rocking	814	815

Table II
Residual Unsaturation and Microstructural Content of the Polymer after Various Conditions of Hydrogenation

sample no.	trans-1,4, %	cis-1,4, %	vinyl, %	residual unsaturation, %
1	50.8	35.3	13.9	100
2	51.8	37.6	10.6	89
3	56.0	38.8	5.2	76
4	66.6	30.3	3.1	50

C–H stretching vibrations. Prominent band features ascribed to aromatic ring vibrations are the absorptions at 1600, 1580, 1500, and 1450 cm^{-1}. The appearance of bands at 1088 and 814 cm^{-1} are assigned to aromatic C–H in-plane bending modes and to an adjacent C–H rocking vibration, which are in agreement with the postulate of a para-disubstituted benzene ring being present. The bands at 1320 and 1140 cm^{-1} are attributed to the C–SO$_2$–C group.

The Raman vibrational data show prominent features assigned to aromatic vibrations. The bands at 3100–3000 cm^{-1} are due to aromatic ring C–H vibrations. The aromatic C–C ring stretching bands are observed at 1600, 1580, 1500, 1450, and 1000 cm^{-1}. The aromatic C–H in-plane bend is seen at 1090 cm^{-1}, and the adjacent C–H rock is seen at 815 cm^{-1}. The bands at 1331 and 1152 cm^{-1} are ascribed to the asymmetric ((C)–SO$_2$–(C)) vibration and the symmetric ((C–)SO$_2$–(C)) vibration, respectively. The SO$_2$ in-plane rock is seen at 509 cm^{-1} and the SO$_2$

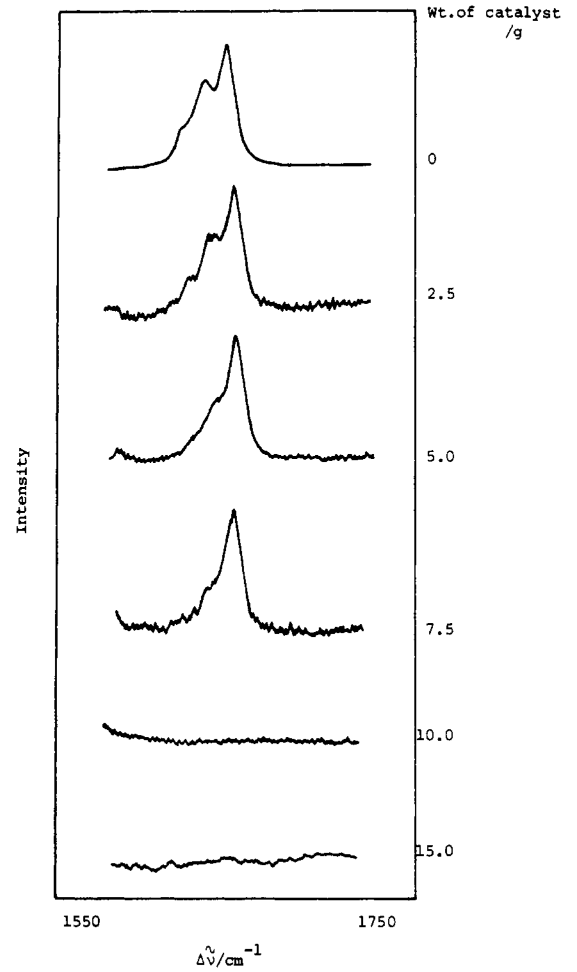

Figure 5. Raman spectra for polybutadienes with different microstructures in the region $\Delta\nu$ = 1550–1750 cm^{-1}, showing the changes in the bands which are used to determine the microstructure.

deformation at 598 cm^{-1}. The SO_2 rock and CSO out-of-plane deformations are both assigned to the feature at 442 cm^{-1}.

The ν(C=C) bands are overlapping in the Raman spectra, but with the aid of the curve analysis program the three bands can be resolved. The use of resolved band areas is an improvement on the original unresolved band-height[1] measurements.

Raman shows quantitatively that the hydrogenation has altered the microstructure of the polymer. On hydrogenation the amount of unsaturation is reduced as expected, but it is also noticeable that the relative amounts of cis-1,4, trans-1,4, and vinyl were altered at the same time (Table II). The vinyl unsaturation, as a percentage of the total unsaturation, has been reduced from 13.9 to 3.0%. This evidence suggests that there is some selectivity in hydrogenation with respect to the vinyl units.

Quantitative measurements were only possible down to 50% reduction in unsaturation since fluorescence problems from the impurity incorporation and reflection problems arising from the surface changes in the sample becoming white masked the Raman spectra. This hydrogenation method, under the correct conditions, was found, by iodination, to completely hydrogenate the polymer and reduce the unsaturation to 0%.

The qualitative vibrational spectroscopic data agree with the ^{1}H NMR data and suggest an impurity incorporation in the polymer.

The spectroscopic evidence presented in this work has shown that partial hydrogenation using a *p*-toluenesulfonyl hydrazide reagent has led to the incorporation of an impurity of the type shown in the polymer chain.

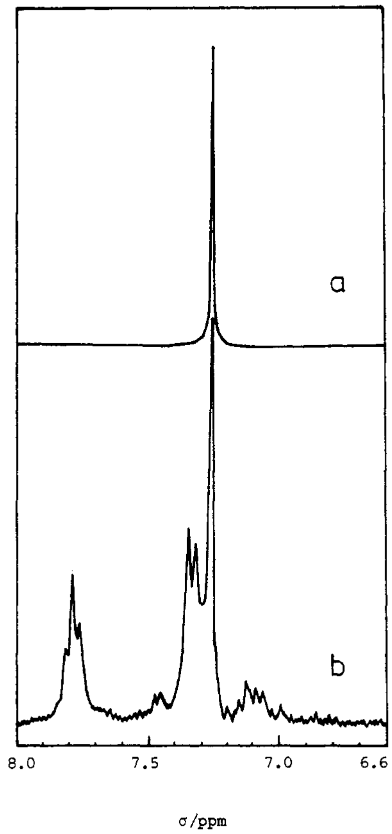

Figure 6. ^{1}H NMR spectrum of the region 6.6–8.6 ppm, showing chemical shift data assigned to a para-disubstituted aromatic compound.

$$CH_3C_6H_4SO_2CH_2CH_2CHRR'$$

The reduction in the vinyl group composition is attributed to a reaction between the vinyl group and the impurity precursor, *p*-toluenesulfinic acid. This reaction, for steric reasons, we ascribe to the favored formation of the transition state between the sulfinic acid and the vinyl group.

The incorporation of this impurity appears to increase with both the amount of *p*-toluenesulfonyl hydrazide used as hydrogenating reagent and the time of hydrogenation. The degree of incorporation has not been studied quantitatively, but due to an increase in the yellow color of the samples the statement that impurity incorporation increases has been made. This is ascribed to the length of exposure of the polymer to the impurity-incorporating precursor.

Conclusion

This work provides evidence for impurity incorporation during hydrogenation using a diimide decomposition reagent.

Raman quantitative microstructure evidence suggests that the double-bond, cis-1,4:trans-1,4:vinyl ratio has been altered by the hydrogenation. This may be attributed to the reagent being only partially selective rather than being fully selective, favoring the vinyl unsaturation before the 1,4 unsaturation. An alternative explanation is that the vinyl unsaturation is being reduced by both hydrogenation and the incorporation reaction, which favors the vinyl site for steric reasons.

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Registry No. $CH_3C_6H_4$-*p*-SO_2NHNH_2, 1576-35-8; polybutadiene (homopolymer), 9003-17-2.