Raman spectroscopic characterization of microstructure of polybutadienes during hydrogenation and hydrobromination reactions

H. G. M. Edwards*, A. F. Johnson, I. R. Lewis and M. A. Macleod
Interdisciplinary Research Centre in Polymer Science and Technology, Chemistry and Chemical Technology, University of Bradford, Richmond Road, Bradford, West Yorkshire, BD7 1DP, UK

The microstructures of hydrogenated polybutadienes produced using different hydrogenation routes, namely the low-temperature hydrogenation using tris(triphenylphosphine)rhodium(I) chloride or platinum black catalysts, have been studied by Raman spectroscopy. The same spectroscopic method has also been used to examine the products formed by a hydrobromination reaction. The selectivity of these methods towards the various microstructural units has been quantitatively examined from observation of the $v(C{=}C)$ stretching vibrations of the *cis*-1,4, *trans*-1,4 and *vinyl*-1,2 components in the polymer. The isolation and spectroscopic characterization of an intermediate formed during the hydrogenation of polybutadienes using tris(triphenylphosphine)rhodium(I) chloride is also reported.

INTRODUCTION

The polymerization of 1,3-butadiene generally gives rise to products that have a mixture of 1,4 and 1,2 structural units. The polymers studied in this work were produced by free-radical-initiated polymerization, which gives rise to a mixture of these different isomeric units.

The quantitative analysis of the 1,4 and 1,2 content of polybutadienes is a relatively simple procedure using Raman spectroscopy[1,2]. In a recent review[3] of the various methods for the spectroscopic determination of the microstructure of polybutadienes, i.e. Raman, infra-red[4,5] and n.m.r.[6-8] (^1H and ^{13}C), the Raman method proved to be the easiest and most versatile, and was also found to give results that were in good agreement with those obtained by ^{13}C n.m.r. The infra-red technique suffers from a number of limitations[3], including component identification and the accidental degeneracy of bands (interference between different structural units on band intensities). Thus, Raman spectroscopy has been used as the preferred method of analysis in the work reported here.

In the first reported Raman spectroscopic study of polybutadienes, Cornell and Koenig[1] quantitatively deduced the microstructure from the $v(C{=}C)$ Raman bands of *vinyl*-1,2, *cis*-1,4 and *trans*-1,4 units at 1640, 1650 and 1664 cm^{-1}, respectively, using peak heights as a measure. This method is not ideal, as there is incomplete resolution of the $v(C{=}C)$ Raman bands arising from the three microstructural components of interest, and the

quantitative interpretation of the spectra is especially difficult when one or more species is in low concentration. Computer-based curve resolution packages now make the quantitative resolution of overlapping spectral peaks and relative area measurements a relatively straightforward task[3], but it is not without problems and should be used with care to ensure that a unique solution is obtained with the optimization procedure adopted.

Hydrogenated polybutadienes are more oxidatively stable than non-hydrogenated polybutadienes and therefore these polymers have a different range of applications. Many hydrogenation methods have been reported: some require harsh conditions, e.g. high temperature and/or high pressure[9]; others involve the use of an expensive catalyst[10]. One method[11,12] relies on the chemical decomposition of a reactive precursor, such as a diimide species generated from *p*-toluenesulfonylhydrazide by the following reaction:

$$CH_3{-}C_6H_4{-}SO_2NH{-}NH_2 \rightarrow$$
$$CH_3{-}C_6H_4{-}SO_2H + NH{=}NH$$
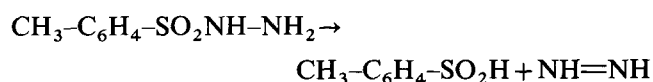
When the polymer is only partially hydrogenated, it has been suggested[12] that a fragment of the reactive precursor may be incorporated[13] into the backbone of the polymer during the hydrogenation process at the *vinyl*-1,2 sites:

$$CH_3C_6H_4SO_2H + H_2C{=}CHCRR' \rightarrow$$
$$CH_3C_6H_4SO_2CH_2CH_2CRR'$$
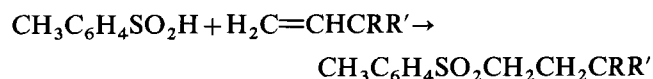
where, for polybutadiene, R and $R' = CH_2$.

It is claimed, on the basis of i.r. and ^1H n.m.r. measurements, that when tris(triphenylphosphine)-

---

rhodium(I) chloride (RhCl(PPh₃)₃) is used as a catalyst for the hydrogenation of polybutadiene[10], the *vinyl*-1,2 units only are selectively hydrogenated.

Platinum black[14] has been used to hydrogenate polybutadiene fully, yielding properties similar to polyethylene for hydrogenated polybutadiene. Partially hydrogenated polybutadienes are analogous to a butene and ethylene copolymer, but have different compositions to materials prepared by direct polymerization.

Hydrobromination is another type of unsaturation modification that not only improves the oxidative stability of the polymer but also leaves the halogen site available for further reaction or functionalization.

In this work, the study of polybutadiene microstructure from two methods of hydrogenation, using tris(triphenyl-phosphine)rhodium(I) chloride and platinum black, and hydrobromination are examined using Raman spectroscopy. Problems related to intermediate incorporation in the reacted polymer and microstructural changes caused by the reactions are discussed.

EXPERIMENTAL

Hydrogenation

Platinum black catalysed reaction (1a). Platinum black (12.5 mg) and cyclohexane (6.0 ml) were admitted to the reaction flask (150 ml) and the mixture was frozen in a carbon dioxide/acetone bath.

A known volume of hydrogen, measured by water displacement, was admitted to the gas reservoir of the evacuated system whilst the reaction flask was isolated. Polybutadiene (Aldrich 25038-44-2, 0.3 ml, $M_w = 4500$), a viscous liquid, was injected into the reaction flask via a serum cap, and hydrogen was admitted from the reservoir. The flask was lowered into a thermostatically controlled bath at 30°C.

The amount of hydrogen taken up was determined, with time, by the change of water level in the reservoir. The experiment was repeated, varying the time of exposure of the polybutadiene to hydrogen, and consequently the amount of hydrogen taken up. Therefore, partially hydrogenated samples could be produced.

Tris(triphenylphosphine)rhodium(I) chloride catalysed reaction (1b). The experiment was repeated as in (1a) but using as the catalyst tris(triphenylphosphine)-rhodium(I) chloride in place of the platinum black. The polybutadiene samples used were from the same batch (Aldrich, 25038-44-2) and the catalyst to polymer ratio was maintained at the same level as used in (1a).

After the hydrogenations the catalysts were removed by filtration and the filtrate was retained for analysis. Samples numbered 1–4 are from the platinum black catalysed hydrogenation (1a), 5–9 are from the tris-(triphenylphosphine)rhodium(I) chloride catalysed hydrogenation (1b) and 10–16 are from the hydrobromination reaction (2).

It should be noted that in the two methods (1a) and (1b), the mechanical shaker agitated the mixture at the same rate throughout the course of the experiments and that an increase in shaking rate causes an increase in the uptake of hydrogen.

Hydrobromination (2)

Polybutadiene (Aldrich, 25038-44-2, 2 g) was dissolved in cyclohexane (150 ml) in a 250 ml two-necked flask. A guard tube containing calcium chloride and molecular sieves (BDH, Type 13X) was attached to one neck of the flask and to the other a gas inlet tube terminated with a glass frit. The solution was heated to 75°C with constant stirring and then hydrogen bromide gas (Aldrich, 29541-8) was passed into the mixture. The reaction was allowed to proceed for 1 h.

The reaction was carried out for both 2 and 3 h with the previously mentioned polybutadiene sample (Aldrich, 25038-44-2) and for 1, 3 and 6 h with another polybutadiene (Aldrich, 18128-2).

Raman spectroscopy

Raman spectroscopic studies were undertaken on two samples of the polybutadiene solutions in cyclohexane mentioned above ((1a) and (2)). Samples were analysed using as the excitation source 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 analysed 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. The number of scans employed was 10 per sample, using a laser power of 500 mW and a spectral slit width of 4 cm^{-1}.

Data acquisition and spectrometer control were effected using a Thorn-EMI PET computer. This facility allowed spectral accumulation to be made over predetermined wavenumber ranges to improve the signal-to-noise ratio. The data were transferred using a customized PET program via the RS 232 interface to an IBM PC. Curve resolution was effected using the 'Lab Calc' (Galactic Industries) software.

The polybutadiene samples from (1b) were orange/red in colour and fluorescence masked the observation of Raman spectra using argon laser excitation. Therefore, these samples were analysed using a Bruker IFS 66 with FRA 106 FT-Raman accessory. These samples were analysed in the solid state. The colour of these samples indicated that incorporation of catalyst intermediates or by-products had occurred.

In obtaining the FT-Raman spectra, 400 scans were accumulated at 4 cm^{-1} resolution using a laser power of 300 mW (focused) over the wavenumber range $\Delta v = 150-3500 \, cm^{-1}$. The laser used in these experiments was a Nd:YAG laser operating at a wavelength of 1064 nm.

The measured band areas of each of the structural units were directly proportional to species concentration[1,3] and, therefore, could be used for quantitative determination of the unsaturation in the polybutadiene samples. As the $v(C=C)$ structural 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:

Percentage of species of microstructure $x = 100[A^x]/[A^{tot}]$

An example of the curve-fitting routine is given in *Figure 1* for a pure polybutadiene homopolymer.

RESULTS AND DISCUSSION

For the heterogeneous hydrogenation reaction involving platinum black, the polymer was hydrogenated until no more hydrogen was taken up. The maximum amount of

hydrogen taken up by the polybutadiene was 72 ml. This corresponds to 3.2×10^{-3} mol of unsaturation removed from a maximum starting unsaturation of 4.9×10^{-3} mol. The uptake of hydrogen during the 72 ml hydrogenation reaction has been displayed graphically in *Figure 2*.

The Raman spectra (*Figure 3*) revealed that the band shapes were similar for the hydrogenated and unhydrogenated samples, and that the microstructural content had remained the same (*Table 1*). This indicated that there has been no selective hydrogenation of the C=C units in the microstructural components.

As stated previously, the hydrogenation using method (1b) produced polymers that were reddish orange in colour, which may be ascribed to some sort of catalyst incorporation. The catalyst could be chemically bound or physically entrapped in these samples. Therefore the Raman spectroscopic study was undertaken to find any evidence of C–Rh bonding. The hydrogenated polymers readily dissolved in hexane but the catalyst could not be recovered. On washing the polymer with absolute alcohol the catalyst was still not removed.

A stack plot of the FT-Raman spectra of the samples from (1b) in the wavenumber range $\Delta v = 1550\text{--}1750\,\mathrm{cm}^{-1}$ is provided in *Figure 4*. From *Figure 4* it can be seen that, owing to the large decrease in the *vinyl*-1,2 band relative to the *trans*-1,4 band, during the hydrogenation the catalyst is partially selective. Band area measurements are given in *Table 2* and it can be seen that the content of the *vinyl*-1,2 group has been reduced with respect to
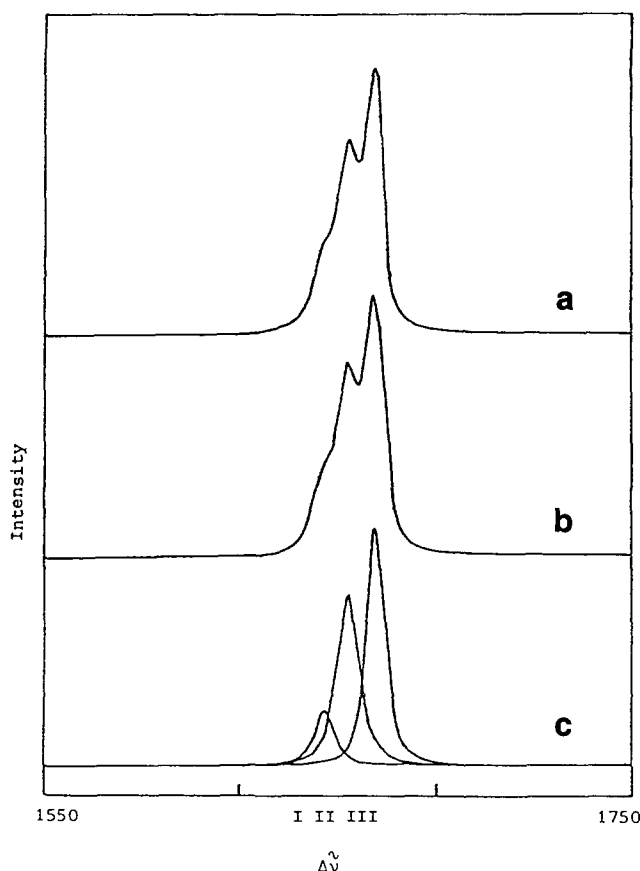

Figure 1 An example of the curve-fitting routine. (a) Recorded spectrum; (b) simulated spectrum; and (c) individual bands used to simulate the total band envelope, (I) *vinyl*-1,2, (II) *cis*-1,4 and (III) *trans*-1,4
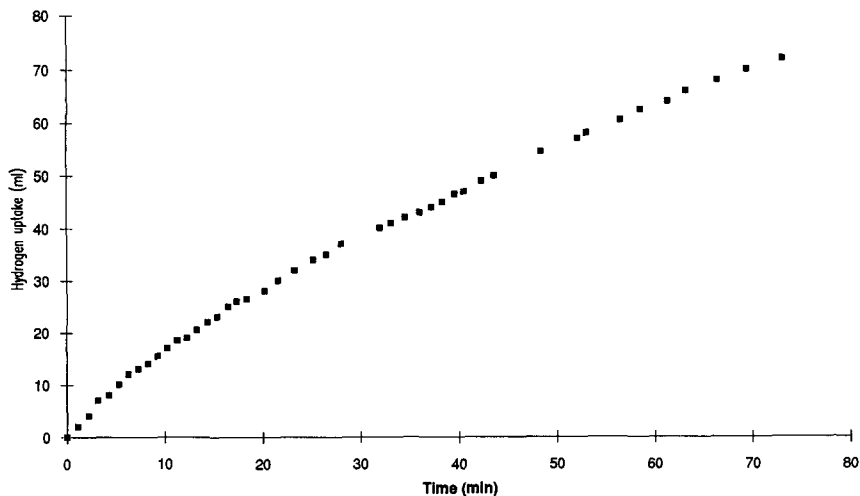
Table 1 Extent of removal of unsaturation and microstructural content of the polymer after hydrogenation with platinum black as the catalyst

Sample no.	*trans*-1,4 (%)	*cis*-1,4 (%)	*vinyl*-1,2 (%)	Moles of unsaturation removed ($\times 10^{-3}$)
1	32	23	45	0
2	29	18	53	1.2
3	36	18	46	1.9
4	32	20	32	3.2

Table 2 Extent of removal of unsaturation and microstructural content of the polymer after hydrogenation with tris(triphenylphosphine)rhodium(I) chloride hydrogenation

Sample no.	*trans*-1,4 (%)	*cis*-1,4 (%)	*vinyl*-1,2 (%)	Moles of unsaturation removed ($\times 10^{-3}$)
5	32	23	45	0
6	37	21	42	0.58
7	39	21	40	1.07
8	43	21	37	1.73
9	52	19	29	2.35

Figure 2 Plot of hydrogen uptake vs. time for the platinum black catalysed hydrogenation reaction
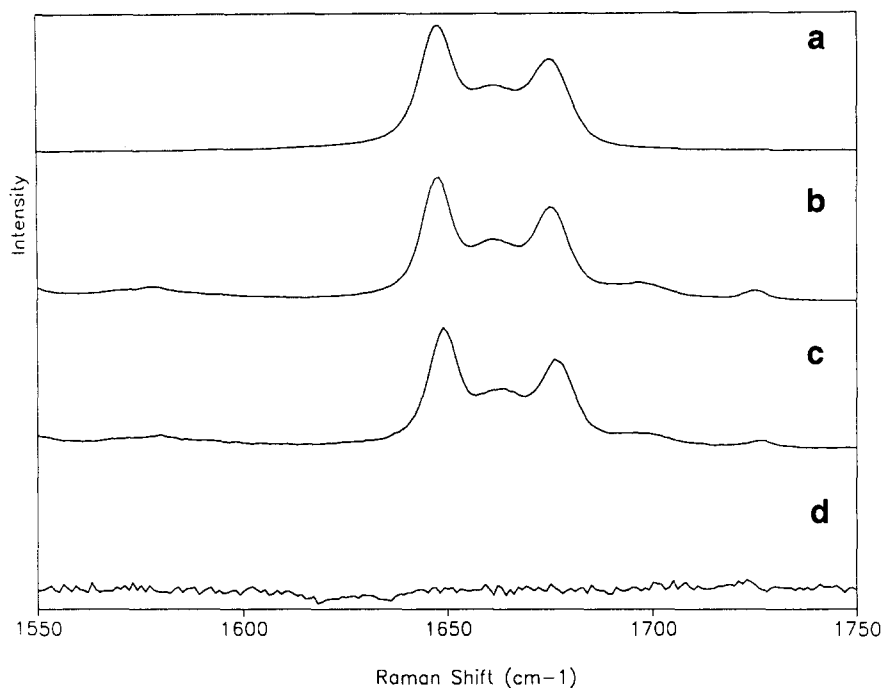
Figure 3 Stack plot of Raman spectra, $\Delta v = 1550$–$1750\,\mathrm{cm}^{-1}$, for (a) unhydrogenated polymer, (b) $1.2 \times 10^{-3}\,\mathrm{mol}$ unsaturation removed, (c) $1.9 \times 10^{-3}\,\mathrm{mol}$ unsaturation removed and (d) $3.2 \times 10^{-3}\,\mathrm{mol}$ unsaturation removed
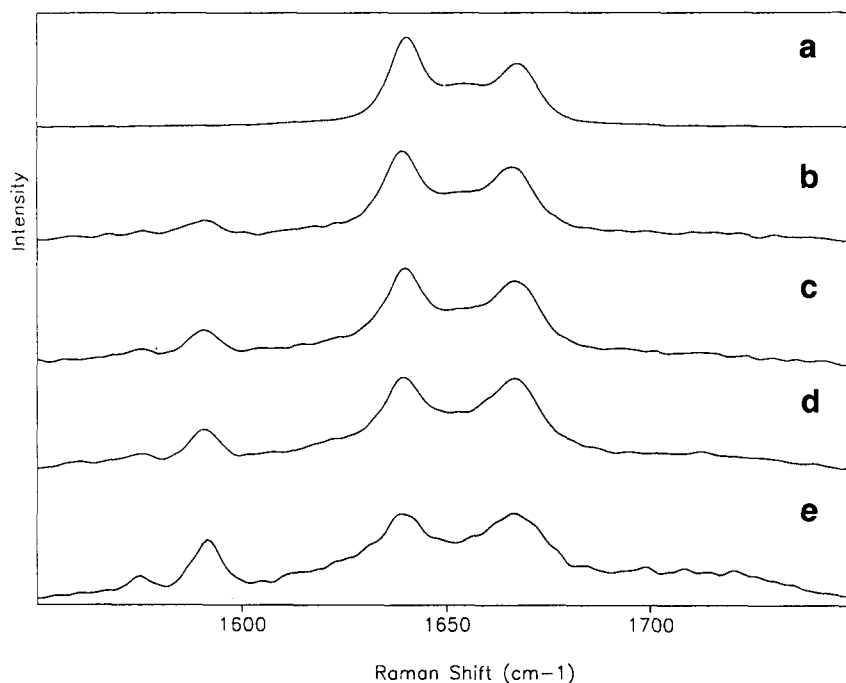
Figure 4 FT-Raman stack plot of the $v(\mathrm{C}{=}\mathrm{C})$ region for (a) unhydrogenated polymer, (b) $5.8 \times 10^{-3}\,\mathrm{mol}$ unsaturation removed, (c) $1.07 \times 10^{-3}\,\mathrm{mol}$ unsaturation removed, (d) $1.73 \times 10^{-3}\,\mathrm{mol}$ unsaturation removed, and (e) $2.35 \times 10^{-3}\,\mathrm{mol}$ unsaturation removed

the 1,4 groups. The distribution of the type of 1,4 units in the total amounts of the 1,4 groups has remained approximately constant during this experiment.

In previous work[10,15] with this catalyst no mention has been made of the polymer being coloured. The observation of some form of incorporation of the catalyst may be important for the use of this system on a large scale. In *Figure 4*, FT-Raman spectra are given of the partially hydrogenated polymer, and it can be seen that a number of new bands appear that may be due to

tris(triphenylphosphine)rhodium(I) chloride. The chemical incorporation of tris(triphenylphosphine)rhodium(I) chloride could not be confirmed without a vibrational assignment of the tris(triphenylphosphine)rhodium(I) chloride, which was not available in the literature.

A possible origin for the impurity, in the hydrogenated polymer, could be physical entrapment occurring during the experimental procedure. If the polymer did not dissolve properly, then the catalyst could become trapped due to a gelling of the polymer, causing the formation

of a viscous polymer mass. The production of a viscous polymer mass coupled with the agitation of the mixture could give rise to physical entrapment of the catalyst, but it would be expected that on dissolution the catalyst could be recovered. This was not observed in practice, and chemical incorporation in accordance with the suggestions of Tolman *et al.*[16] is the most likely explanation for the colour of the reaction products.

From the Raman assignments of tris(triphenylphosphine)rhodium(I) chloride[17], new bands ascribed to the incorporated material (*Figure 5*) can be observed and are summarized in *Table 3*.

In tris(triphenylphosphine)rhodium(I) chloride[17] there are two u X-sensitive bands at 260 and 245 cm^{-1}, where the 260 cm^{-1} band is of higher intensity (*Figure 6c*). These u X-sensitive vibrations are related to a C–P deformation[17]. The band observed in the incorporated material (sample 7) (*Figure 6b*) is broad and is centred at 249 cm^{-1}. This band is of higher intensity than those of tris(triphenylphosphine)rhodium(I) chloride and both
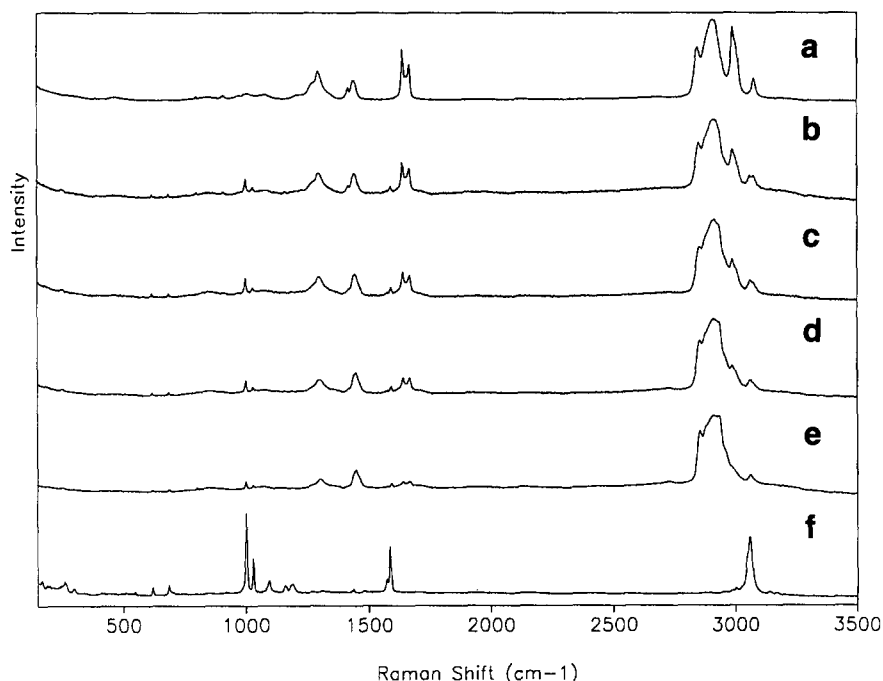

Figure 5 FT-Raman stack plot of the ν(C=C) region for (a) unhydrogenated polymer, (b) 5.8 × 10^{-3} mol unsaturation removed, (c) 1.07 × 10^{-3} mol unsaturation removed, (d) 1.73 × 10^{-3} mol unsaturation removed, (e) 2.35 × 10^{-3} mol unsaturation removed and (f) tris(triphenylphosphine)rhodium(I) chloride
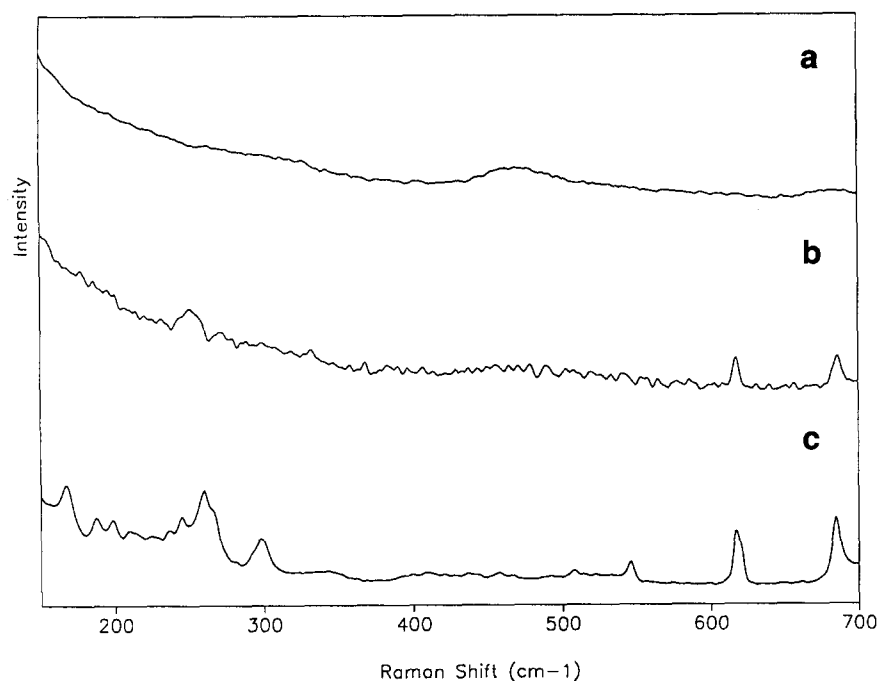

Figure 6 FT-Raman spectra in the wavenumber range $\Delta\nu = 150$–700 cm^{-1} for (a) unhydrogenated polymer, (b) partially hydrogenated polymer (sample 7) and (c) tris(triphenylphosphine)rhodium(I) chloride

Table 3 FT-Raman wavenumbers and assignments of new bands observed after hydrogenation of polybutadiene using tris(triphenylphosphine)rhodium(I) chloride

Observed wavenumbers (cm^{-1})	Approximate description of vibrational mode[17]
3059	ν(C–H)
1591	k ν(C–C) aromatic
1578	l ν(C–C) aromatic
1028	b δ(C–H)$_{ip}$
1000	p ring breathing
685	r X-sensitive
617	s δ(C–C)$_{ip}$ ring
249	ν(Rh–C)

ip, in-plane deformation
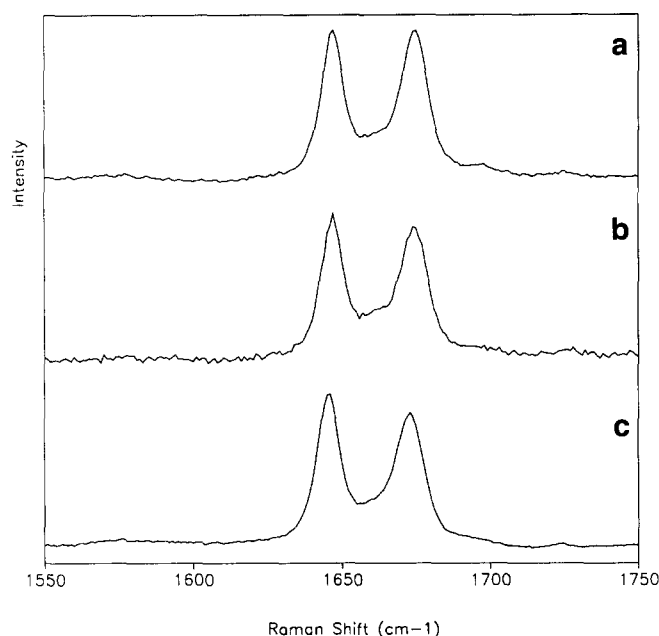
Figure 7 Stack plot of the Raman spectra, $\Delta\nu = 1550$–$1750\,\mathrm{cm}^{-1}$, for the medium *vinyl*-1,2 polybutadiene after hydrobromination for (a) 1 h, (b) 2 h and (c) 3 h

the u X-sensitive bands, and may be assigned to the Rh–C stretch.

The M–C stretching vibrations in metal alkyls are normally observed[18] above $400\,\mathrm{cm}^{-1}$. However, the assignment to the lower wavenumber of $249\,\mathrm{cm}^{-1}$ here is related to the mass of the polymer chain. In PdMe$_2$(PEt$_3$)$_2$ the ethyl group is light and the vibration is observed[18] at $491\,\mathrm{cm}^{-1}$. In PdMe$_2$(PPh$_3$)$_2$ the ethyl groups are replaced by heavier phenyl rings and the Pd–C stretching vibration is shifted to a lower-wavenumber position, $482\,\mathrm{cm}^{-1}$. In this case, the molecule is RhCl(PPh$_3$)$_2$ CHR, where the relative molecular mass of the CHR unit is 4500. This extra mass could cause the Rh–C vibration to be observed outside its normal range; also the Rh–C bond could be weaker than that in the simple Pd–C system.

The extent of catalyst incorporation has been estimated from the intensity of the $1000\,\mathrm{cm}^{-1}$ band, aromatic ring stretch, in the pure complex and in the polymer, and is found to be less than 10% for all hydrogenated samples.

Although the method is partially selective for the *vinyl* group, the incorporation of the catalyst detracts from its potential usefulness in hydrogenations of the C=C bond.

Figures 7 and *8* show the Raman spectra of the two hydrobrominated polybutadiene samples. The

microstructural measurements are given in *Table 4*. From *Table 4* it can be seen spectroscopically that no significant selectivity is observed in the hydrobromination, which is in agreement with theory[19]. From the intensity of the ν(C=C) stretching vibration relative to the solvent band, at $1446\,\mathrm{cm}^{-1}$, it was determined that the level of unsaturation had been reduced to approximately 50%. At this level it was still possible to investigate the solution using argon laser excitation.

CONCLUSIONS

The method of hydrogenation using platinum black was clean, no impurity problems were observed, and the acquisition of spectra was not complicated by fluorescence problems. This method can be recommended for full and partial hydrogenations of polybutadiene. Partial hydrogenation using tris(triphenylphosphine)-rhodium(I) chloride produces incorporation of the catalyst by the mechanism proposed by Tolman *et al.*[16] and fluorescence masks the argon-excited Raman spectrum. Nd:YAG-excited Raman spectra have been used to determine that the hydrogenation reaction is only partially selective for the *vinyl* group and not fully selective as suggested by previous authors[10]. It has also been successfully shown that Raman spectroscopy can be used to study quantitatively the
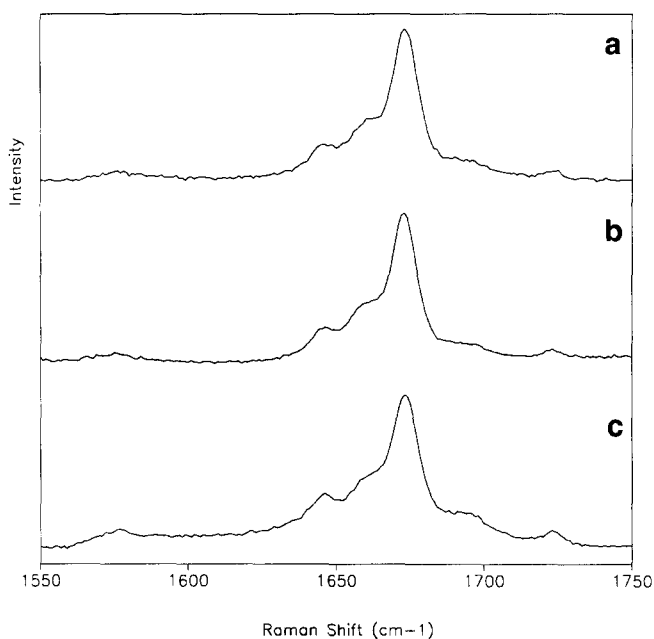

Figure 8 Stack plot of the Raman spectra, $\Delta\nu = 1550$–$1750\,\mathrm{cm}^{-1}$, for the low *vinyl*-1,2 polybutadiene after hydrobromination for (a) 1 h, (b) 3 h and (c) 6 h

Table 4 Microstructural content of the polymer after different lengths of hydrobromination

Sample no.	*trans*-1,4 (%)	*cis*-1,4 (%)	*vinyl*-1,2 (%)	Time (h)
10	47	8	45	1
11	47	9	44	2
12	45	9	46	3
13	60	28	12	0
14	64	19	17	1
15	67	18	15	3
16	59	19	22	6

distribution of microstructure units in polybutadienes after hydrobromination reaction up to an estimated loss of 50% in unsaturation.

REFERENCES

1   Cornell, S. W. and Koenig, J. L. *Macromolecules* 1969, **2**, 540
2   Poshyachinda, S., Edwards, H. G. M. and Johnson, A. F. *Polymer* 1991, **32**, 338
3   Frankland, J. A., Edwards, H. G. M., Johnson, A. F., Lewis, I. R. and Poshyachinda, S. *Spectrochim. Acta (A)* 1991, **47**, 1511
4   Silas, R. S., Yates, J. and Thornton, V. *Anal. Chem.* 1959, **31**, 529
5   Haslam, J., Willis, H. A. and Squirrel, D. C. M. 'Identification and Analysis of Plastics', 2nd Edn., Butterworth, London, 1972
6   Harwood, H. J. *Rubber Chem. Technol.* 1982, **55**, 769
7   Elgert, K.-F., Quack, G. and Stutzel, B. *Polymer* 1975, **16**, 154
8   Van der Velden, G., Didden, C., Veermans, T. and Beulen, J. *Macromolecules* 1987, **20**, 1252
9   Rachapudy, H., Smith, G. G., Raju, V. R. and Graessley, W. W. *J. Polym. Sci., Polym. Phys. Edn.* 1979, **17**, 1211
10 Mohammadi, N. A. and Rempel, G. L. *J. Mol. Catal.* 1989, **50**, 259
11 Mango, L. A. and Lenz, R. W. *Makromol. Chem.* 1973, **163**, 13
12 Harwood, H. J., Russel, D. B., Verthe, J. J. A. and Zymonas, J. *Makromol. Chem.* 1973, **163**, 1
13 Edwards, H. G. M., Johnson, A. F., Lewis, I. R., Ward, N. J. and Webb, N. *Macromolecules* 1992, **25**, 525
14 Camberlin, Y., Pascault, J. P., Razzouk, H. and Cheradure, H. *Makromol. Chem., Rapid Commun.* 1981, **2**, 323
15 Doi, Y., Yana, A., Soga, K. and Burfield, D. R. *Macromolecules* 1986, **19**, 2409
16 Tolman, C. A., Meakin, P. Z., Linder, D. L. and Jesson, J. P. *J. Am. Chem. Soc.* 1974, **96**, 2762
17 Edwards, H. G. M., Johnson, A. F. and Lewis, I. R. *Spectrochim. Acta* in press
18 Adams, D. M. 'Metal–Ligand and Related Vibrations', Edward Arnold, London, 1967
19 Vogel, A. I. 'Elementary Practical Organic Chemistry', 3rd Edn., Longman, London, 1980