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FT Raman spectroscopic study of the diimide hydrogenation of *cis*-polybutadiene: some evidence of *cis–trans* isomerization

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Abstract—The diimide hydrogenation of *cis*-polybutadiene is studied. *p*-Toluenesulfonylhydrazide is used to fully and partially hydrogenate *cis*-polybutadiene. The microstructure and hydrogenation of the samples obtained are subsequently studied by FT Raman spectroscopy. *Cis–trans* isomerization is found to take place during the reaction. A mechanism of isomerization and hydrogenation is also proposed.

Keywords: Polybutadiene, hydrogenation, FT Raman spectroscopy, *cis–trans* isomerization.

INTRODUCTION

CATALYTIC hydrogenation has been found to be a useful tool for the reduction of unsaturation in olefins and diene polymers [1–4]. However, such heterogeneous systems result in difficulties when handling the reactions, usually involving high pressures and temperatures. Hydrogenation using diimide [5–9] has been found to be relatively simpler since it can be carried out at atmospheric pressure and moderate temperatures. Moreover, the reactions take place under homogeneous conditions and pose no problem in the separation of polymer from the catalyst.

Cis–trans isomerization in olefins during hydrogenation has been observed to be dependent on the nature of the catalysts used [1, 2]. Catalysts such as palladium produce extensive isomerization [1] whereas platinum oxide tends to produce very little isomerization [2]. In the previous work [10], UV radiation was also used successfully to induce *cis–trans* isomerization in polybutadienes in the presence of organobromide, sulfide, disulfide or mercaptan.

The microstructure of polybutadienes can be determined quantitatively by Raman spectroscopy [11–14] since the $\nu(C{=}C)$ stretching vibrations of *cis*, *trans* and vinyl units are strongly active and appear at different frequencies. Accuracy and ease of operation result in Raman spectroscopy being favoured over the other spectroscopic techniques [14].

In this work, a diimide releasing agent, *p*-toluenesulfonylhydrazide (TSH), is utilized in order to partially and fully hydrogenate *cis*-polybutadiene. The microstructures of the samples involved are subsequently characterized and studied by FT Raman spectroscopy.

EXPERIMENTAL

Syntheses

The hydrogenation of *cis*-polybutadiene samples was carried out as follows; about 1.0 g of *cis*-polybutadiene was dissolved in 120 ml of xylene (Merck) which was previously dried over 4 Å

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molecular sieves. A certain amount of *p*-toluenesulfonylhydrazide (TSH) (Fluka) was then added to the solution to obtain a molar ratio of TSH to double bond ([TSH]/[C=C]) of 2.0. The solution was then stirred and heated to the reflux temperature of xylene (~132 °C) for 4 h. The hydrogenated polymer was subsequently retrieved by precipitating in ethanol and later dried in the vacuum oven for further characterization. Various partially hydrogenated samples were prepared by varying the amount of TSH used to obtain [TSH]/[C=C] of 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4 and 1.6.

FT Raman spectroscopy

The FT Raman spectrometer employed in this work was a PC controlled Perkin Elmer series 2000 FTIR optical unit equipped with a near infrared Nd:YAG laser source and an InGaAs detector. Solid samples were excited at 180° backscattering mode using laser power output of 500 mW. Each sample was scanned 30 times in order to obtain a good signal-to-noise ratio over the range 3600–200 cm^{-1} at 4 cm^{-1} resolution. Quantitative determination of microstructure of the samples obtained was carried out according to the method described elsewhere [14].

RESULTS AND DISCUSSION

Calculation of percentage hydrogenation and microstructure

FT Raman spectra of hydrogenated *cis*-polybutadienes (HGPB) in the region 1750–1350 cm^{-1} can be utilized to determine the achieved percentage hydrogenation of the samples. Since the ν(C=C) bands of vinyl, *cis* and *trans* microstructural units are all strongly Raman active at 1641, 1652 and 1667 cm^{-1}, respectively, the areas of computer resolved bands can be used to determine the percentage of each microstructure in the polymer. In such a case no calibration or internal standard is needed because the total of the three microstructures is taken to be 100. However, the percentage hydrogenation of

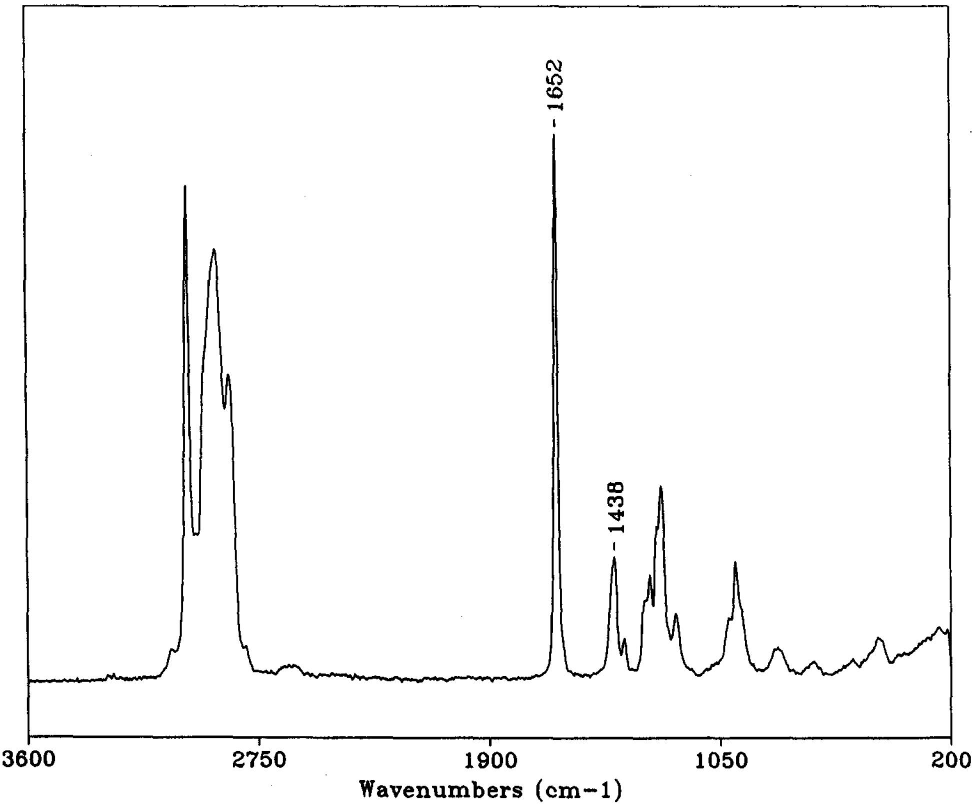

Fig. 1. FT Raman spectrum of solid *cis*-polybutadiene.