Raman spectroscopic characterization of high-vinyl polybutadienes produced from anionic polymerization

Saran Poshyachinda, Howell G. M. Edwards* and Anthony F. Johnson
Chemistry and Chemical Technology, Department of Chemical Engineering, University of Bradford, Bradford, West Yorkshire BD7 1DP

(Received 6 January 1990; accepted 2 March 1990)

High-vinyl polybutadienes have been prepared by anionic polymerization using n-butyllithium as initiator in cyclohexane solvent and complexing agents in order to change the mode of addition of monomer to (1,2)- or vinyl addition. The microstructure of these polymers was characterized by Raman spectroscopy using the Raman active carbon–carbon double bond stretching bands of vinyl, *cis* and *trans* structures at 1640, 1650 and 1664 cm^{-1}, respectively. Band areas were analysed with the aid of a curve analysis program and the data thus acquired used for subsequent calculations. The living-end concentration was determined from the number average molecular weight of the polymer obtained by gel permeation chromatography, which made it possible to calculate a more accurate value for the molar ratio, r, of the complexing agent to living polyanions than is possible by more conventional means. It has been observed that 1,2-dipiperidinoethane (DIPIP) is a very effective complexing agent for the control of polymer microstructure as is diglyme at 0°C but their effectiveness decreases with increasing temperature.

(Keywords: anionic polymerization; high-vinyl polybutadiene; Raman spectroscopy; complexing agent; microstructure)

INTRODUCTION

The polymerization of (1,3)-butadiene gives rise to products which have a (1,4)-polybutadiene or (1,2)-polybutadiene structure or a mixture of these. The (1,4)-addition products may comprise the *cis* or *trans* isomer while the (1,2)-addition may be isotactic, syndiotactic or atactic, or some mixture of these structural types (*Figure 1*).

Anionic polymerization of butadiene in non-polar media with alkyllithium initiators results in polybutadienes with low-vinyl content. Langer[1] found that the introduction of a relatively small amount of *N,N,N',N'*-tetramethylethylenediamine (TMEDA) into the polymerizing solution gave rise to polybutadienes with a predominantly vinyl microstructure with atactic pendant vinyl groups. It is thought that TMEDA forms a complex with living polybutadienyllithium chain ends and changes the mode of addition of monomer from primarily (1,4)- to (1,2)-addition. Antkowiak *et al.*[2] reported the effects of temperature and concentration of complexing agent on the microstructure of the resulting polybutadienes as characterized by infrared spectroscopy. Polybutadienes with vinyl microstructure as high as 80% can be obtained using diglyme as the complexing agent at 30°C. Later, 1,2-dipiperidinoethane (DIPIP) was found to be the most effective complexing agent for butadiene polymerization[3,4].

Determination of the microstructure of polybutadienes by infrared spectroscopy is not simple because the method requires calibration and, more importantly, the carbon–carbon double bond stretching vibration, ν(C=C), of a *trans* unit is infrared inactive. Therefore, the infrared absorption of the skeletal backbone of the polybutadienes cannot be used and carbon–hydrogen deformations of the three microstructures were selected for the analyses[5]. Cornell *et al.*[6] reported the first Raman spectroscopic studies of polybutadienes. The microstructure was quantitatively determined from the ν(C=C) Raman bands of vinyl, *cis* and *trans* units at 1640, 1650 and 1664 cm^{-1}, respectively, from peak height determination. This method suffered from the inherent disadvantage that derives from the incomplete resolution of the ν(C=C) Raman bands arising from the three microstructures, especially when one or more of the components is in a low species concentration.

In this work we report the use of Raman spectroscopy for the microstructure determination of high-vinyl polybutadienes produced anionically in cyclohexane using an alkyllithium initiator with different complexing agents. A curve analysis program applied to the computerized data acquisition enables the band areas of each component band to be evaluated and makes it possible to obtain accurate microstructure compositions from samples which contain relatively small amounts of one or more components. In addition, laser excitation of the Raman spectra gives a means of testing sample homogeneity and surface microstructure composition.

EXPERIMENTAL

The experiments were carried out under high vacuum using well established techniques[7] which have been described fully in an earlier paper[8]. The solvent, cyclohexane (May and Baker, h.p.l.c. grade), was distilled from n-butyllithium prior to use. (1,3)-Butadiene (Aldrich) was also freshly distilled from n-butyllithium into the reaction vessel. The complexing agents, diglyme (Aldrich) and

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* To whom correspondence should be addressed

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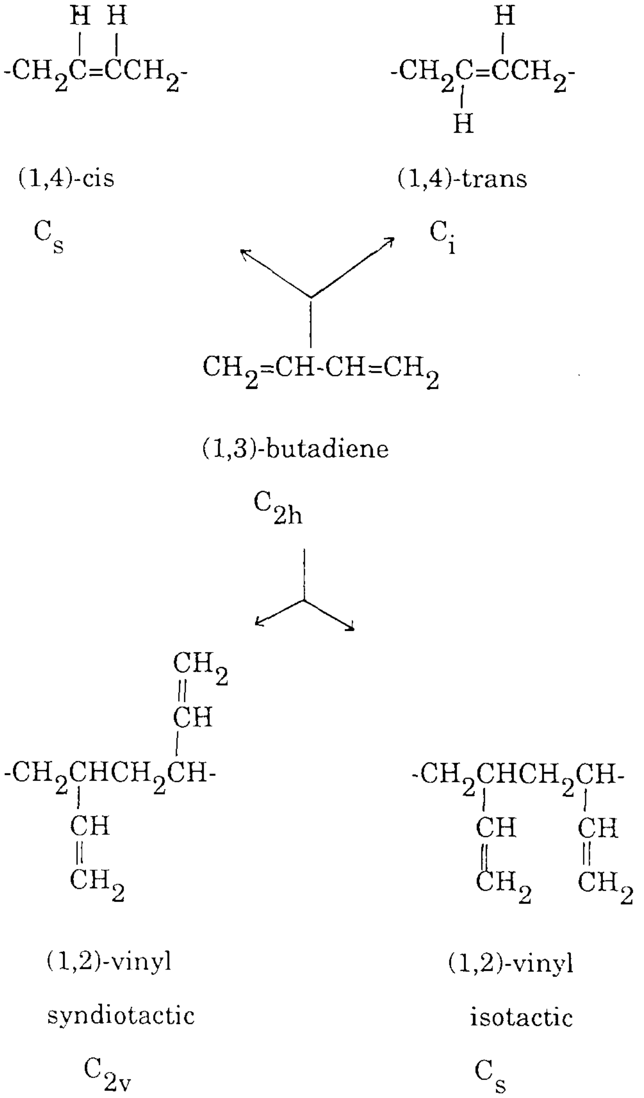

Figure 1 Polymerization routes for (1,3)-butadiene. Local molecular symmetry point groups are also shown

1,2-dipiperidinoethane (DIPIP), were dried over CaH_2 under vacuum for at least 2 weeks before use. The n-butyllithium (Aldrich) initiator was used as supplied apart from dilution with cyclohexane.

Polybutadienes with high-vinyl content were produced by polymerizing butadiene in cyclohexane. The presence of complexing agents resulted in the mode being largely (1,2)-addition. The reactions were carried out at 0°C and 30°C, and the molar ratio of complexing agent to lithium, $r = [\text{complexing agent}]/[\text{Li}]$, was varied with [Li] controlled at 10^{-3} molar. Monoglyme, diglyme, triglyme, DIPIP, TMEDA and *N*,*N*,*N*′,*N*′-tetraethylethylenediamine (TEEDA) were used as complexing agents in this work.

Because fast initiation rates relative to propagation rates can be achieved in these reactions with added complexing agent[4], low polydispersity polymers are obtained. Assuming that all molecules are of the same length, the molecular weight of the polymer can be related directly to the concentration of initiator in the polymerizing solution, i.e. $\text{DP} = [\text{monomer}]/[\text{Li}]$. Therefore, molecular weight determination can be used in order to obtain the effective concentration of the initiator, and hence, the *r* value.

In this work, gel permeation chromatography (g.p.c.) was used to determine the number average molecular weight ($\bar{M}_n$) of the polymers. Two Polymer Laboratories gel mixed bed columns with a 10 μm bead diameter were employed with tetrahydrofuran as the eluant. The columns were calibrated with low-vinyl polybutadiene standards and Mark–Houwink constants, obtained from Anderson *et al.*[9], were used in order to calculate the molecular weight of the high-vinyl samples based on the universal calibration theory. Analyses were carried out with an eluant flow rate of 1 ml min^{-1} and raw data were collected and processed by a software package developed in our own laboratories[10].

Raman spectroscopy

Raman spectra of the polybutadiene samples were excited using a Spectra-Physics 2020/5 argon-ion laser with a nominal output power of 1.5 W at 488.0 nm and a Spex 1401 double monochromator with an EMI 9789 QA photomultiplier and a reciprocal linear dispersion of 21.5 $\text{cm}^{-1}\ \text{mm}^{-1}$ at 488.0 nm in the first order. Spectral slit widths of 4 cm^{-1} were employed and the Raman line wavenumber shifts were calibrated using the emission lines of a neon lamp. The wavenumber shifts of observed Raman lines are correct to $\pm 1\ \text{cm}^{-1}$. Spectrometer control was effected using a Nicolet 1180 computer which facilitated the multiple scanning of spectral ranges, typically $\Delta\tilde{\nu} = 1550$ to 1750 cm^{-1} for the ν(C=C) region of the polybutadienes, and improved signal-to-noise ratios over those of single-scan spectra.

A standard curve analysis package (CAP) enabled the resolution of the ν(C=C) bands in the predetermined spectral region to be effected and band areas determined.

The linearity of response of the spectroscopic apparatus has previously been verified[11], using systems of known internal-field effects and a geometric–optical effect[12] of 1 was determined. For the quantitative analysis of the polybutadiene samples studied in this work, the measured band area was therefore directly proportional to species concentration. Because all three types of microstructure have active ν(C=C) Raman bands in the spectral region under investigation, the ratio of the measured area of species *x*, $[A^x_{\text{obs}}]$, to the total area of the band envelope, $[A^{\text{tot}}_{\text{obs}}]$, represents the percentage composition of the species in the polybutadiene sample: i.e. % species *x* in microstructure $= 100[A^x_{\text{obs}}]/[A^{\text{tot}}_{\text{obs}}]$.

Reproducibility tests were carried out by scanning the same part of the polybutadiene sample several times and working-up the results independently. It is estimated that the compositions are accurate to better than ±1%. Within this experimental error of measurement, no sample inhomogeneities were detected in the recording of microstructure compositions from different regions of the same samples.

RESULTS AND DISCUSSION

The high-vinyl polybutadienes obtained in this work are colourless liquids and solids with a number average molecular weight ($\bar{M}_n$) range between 20 000 to 100 000, as characterized by g.p.c. The polydispersity indices of all polymers were determined to be lower than 1.15 and in most cases are below 1.10, indicating that fast initiation had been achieved in the presence of complexing agent[4]. The measured $\bar{M}_n$ was used for the calculation of *r* values from known amounts of complexing agents. This method for the determination of initiator concentration we believe to be preferential to the more conventional titration of the initiator because it determines the effective concentration and circumvents the problem of killing of the living ends due to impurities in the system.

Microstructure analyses as characterized by Raman spectroscopy for high-vinyl polybutadienes initiated by n-BuLi/diglyme and n-BuLi/DIPIP are shown in *Figures* *2* to *5*. It can be seen that at 30°C DIPIP is more effective than diglyme in promoting a high-vinyl polymerization and samples with as high as 92% vinyl microstructure can be prepared. For diglyme, only 80% vinyl content in the final polymer can be obtained. However, it should be noted in *Figures 3* and *5* that, as the *r* value increases, the proportion of vinyl content of diglyme-complexed chain-ends reaches a plateau before that of DIPIP. Although the same trend is observed at 0°C, as seen in *Figures 2* and *4*, the difference in vinyl content of the polymers produced from diglyme and DIPIP is not as significant as that of the polymers produced at 30°C.

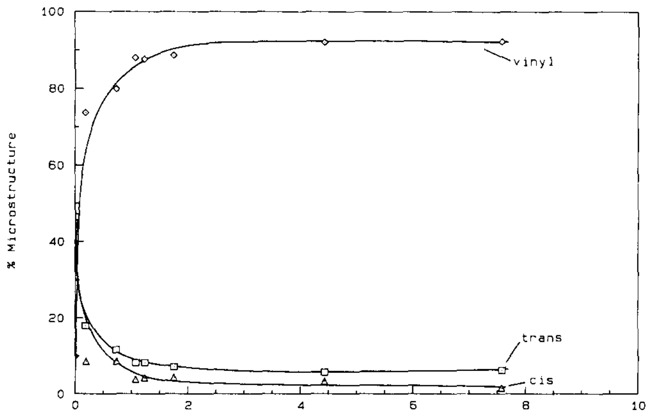

Figure 2 Per cent microstructure of high-vinyl polybutadiene initiated by n-BuLi/diglyme at 0°C

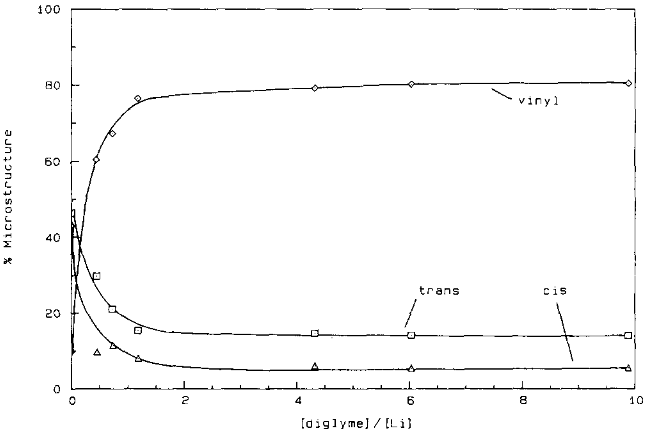

Figure 3 Per cent microstructure of high-vinyl polybutadiene initiated by n-BuLi/diglyme at 30°C

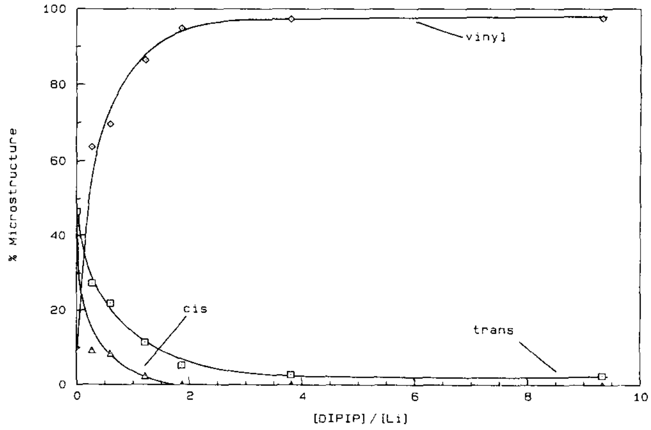

Figure 4 Per cent microstructure of high-vinyl polybutadiene initiated by n-BuLi/DIPIP at 0°C

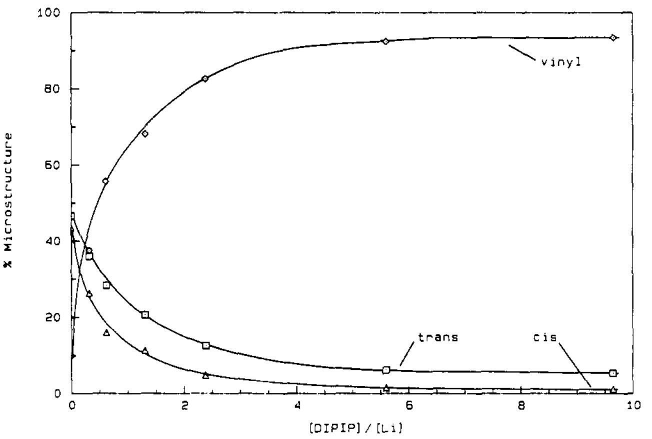

Figure 5 Per cent microstructure of high-vinyl polybutadiene initiated by n-BuLi/DIPIP at 30°C

The highest vinyl content achieved in this work is 97% with DIPIP as complexing agent at *r* values greater than 2. In the case of diglyme at 0°C, 92% vinyl microstructure is achieved at *r* values greater than 1.5.

It is suggested that both steric effects and the strength of the ligand bonding are important factors in dictating the mode of addition of the monomer to the living chain-ends. When the living polybutadienyllithium chain-end is complexed by a ligand such as diglyme, the negative charge distribution over the allylic chain-end is affected. The electron density shifts towards the γ-carbon atom of the complexed chain-end, as characterized by ^{13}C n.m.r. (ref. 13), then favours the addition of monomer to this γ-carbon. As the temperature increases, the dissociation of the complex is favoured and, as a result, the charge density at the γ-carbon atom and the vinyl content decrease. However, Worsfold *et al.*[13] have shown that the effects of TMEDA and DIPIP on the charge distribution of polybutadienyllithium chain-ends are very similar but DIPIP is distinctly more effective in producing high-vinyl polybutadienes. This effectiveness of DIPIP has been ascribed to the steric hindrance of the DIPIP molecule[3].

The major advantages of Raman spectroscopy to infrared spectroscopy for microstructure determination of polybutadienes is that the *cis* and *trans* content can be obtained easily from the same ν(C=C) region and the intensity of the ν(C=C) bands are linear with concentration of species to a first approximation. In all cases the *trans* contents are higher than the *cis*, and in particular, for DIPIP at 0°C, no *cis* band can be seen in the curve-analysed spectra of the polymers with *r* values higher than 2. The absence of *cis* units in these polymers supports the results from n.m.r.[13] that the active centres in the presence of DIPIP are largely in a *trans*

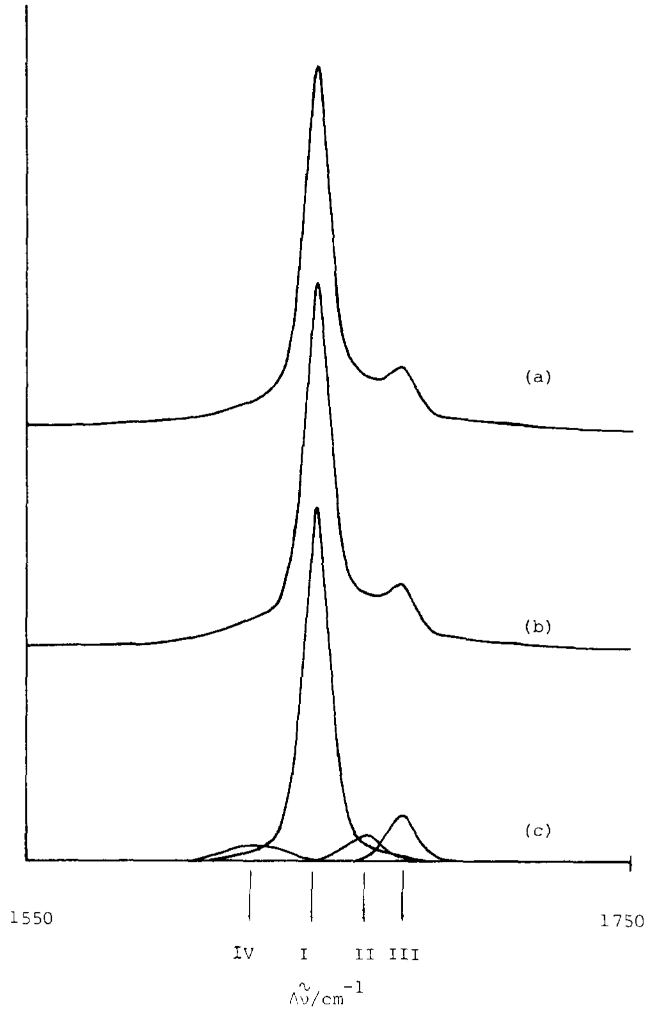

Figure 6 Raman spectrum of high-vinyl polybutadiene initiated by n-BuLi/diglyme at $r = 0.73$: curve a, observed spectrum; curve b, computer calculated; curve c, resolved spectrum: I vinyl, II *cis*-, III, *trans*-microstructure, and IV first overtone of CH_2 rocking mode of pendant vinyl group

Table 1 Per cent microstructure of high-vinyl polybutadienes obtained using different complexing agents

Complexing agent	Temperature °C	*r*	% microstructure vinyl	*cis*	*trans*
Monoglyme	0	6.8	77.0	10.0	13.0
Triglyme	0	5.2	91.0	3.1	5.9
Triglyme	30	5.8	82.1	6.7	11.2
TMEDA	0	7.2	79.9	8.3	11.8
TEEDA	0	6.4	83.8	3.8	12.4

configuration at larger *r* values, for example 93% at $r = 2.10$. Hence *trans*-addition takes place when the *trans* living end is frozen by the next (1,4)-addition of the new monomer molecule.

It should be noted that a new feature appears in the Raman spectra of high-vinyl samples (*Figure 6*) as a broad, weak band at $\Delta\tilde{\nu} = 1618\text{–}1620\ \mathrm{cm}^{-1}$. This has not been reported before. The origin of this band may be directly ascribed to the vinyl groups in the atactic high-vinyl polybutadiene since the band intensity increases with vinyl content of the sample. There is a medium-strong intensity band at $\Delta\tilde{\nu} = 801\ \mathrm{cm}^{-1}$ in high-vinyl samples which has a similar intensity behaviour. The weak feature at $\Delta\tilde{\nu} = 1618\text{–}1620\ \mathrm{cm}^{-1}$ may thus be assigned to the first overtone of the $\Delta\tilde{\nu} = 801\ \mathrm{cm}^{-1}$ band. Calculations show that the harmonic wave number of the fundamental band, $\tilde{w}_e = 784\ \mathrm{cm}^{-1}$, and the anharmonicity, $x_e = -0.01$. With regard to the fundamental at $\Delta\tilde{\nu} = 801\ \mathrm{cm}^{-1}$ in high-vinyl polybutadiene samples, because this band is absent from *cis* and *trans* polybutadienes it may be confidently assigned to a $CH_2{=}CH$-pendant vinyl group mode. However, (1,3)-butadiene[14], vinyl mercury (II) halides[15] and divinyl mercury (II)[15,16] do not have fundamental bands near $800\ \mathrm{cm}^{-1}$ for similar vinyl groupings. In divinyl mercury (II)[15] the Raman fundamental at $\Delta\tilde{\nu} = 1578\ \mathrm{cm}^{-1}$ has been assigned to $\nu(C{=}C)$ stretching and a weak feature at $1614\ \mathrm{cm}^{-1}$ is unassigned, whereas another at $1652\ \mathrm{cm}^{-1}$ has been assigned to a combination band of skeletal stretching and CH_2 deformation modes. We would tentatively assign the band at $801\ \mathrm{cm}^{-1}$ in our spectra to a vinyl CH_2 rocking mode or CH_2 scissors deformation and the $1618\ \mathrm{cm}^{-1}$ band to its first overtone. An alternative assignment would give the $1618\ \mathrm{cm}^{-1}$ band as a combination of a skeletal stretching mode and a vinyl CH_2 deformation, by analogy with vinyl mercury (II) compounds.

Table 1 shows the microstructure of the highest vinyl-content polybutadienes produced using several complexing agents. These complexing agents are not as effective as DIPIP and diglyme at 0°C. In comparison with the published data in the case of diglyme at 30°C, the highest vinyl-content closely agrees with those reported by Antkowiak *et al.*[2] for which no data are available at 0°C. For DIPIP, data reported at 5°C by Bywater *et al.*[4] and this work at 0°C agree very closely in the highest vinyl-content but do not agree in the *r* values for which the polymers were produced. The vinyl content/*r* curve at 5°C reaches a plateau at an *r* value higher than 1, whereas in the present work the same stage is reached at $r > 2$. The most likely explanation for this discrepancy lies in the method used for the determination of the *r* value, which, in the present work, is measured by the effective concentration of the lithium.

ACKNOWLEDGEMENT

We thank the Institute for the Promotion of Teaching Science and Technology, Thailand, for a research studentship to S. Poshyachinda.

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