two to three units and longer. This is much more sensitive than the chemical osmium tetroxide method. For example the chemical method detected only 1.3% block styrene for samples 4 and 5 and 4.3% for sample 7. Except for sample 1 the nmr method gave quite reasonable results.

This method has the potential of yielding information about the styrene sequences from the shape of the aromatic resonance and its resolution into its separate peaks in butadiene–styrene copolymers and in other styrene-containing copolymers. The technique should also prove extremely useful in obtaining sequence distribution information in other copolymer systems or in tacticity studies in which the resolution of overlapped peaks is important.

Acknowledgments. We wish to thank H. J. Harwood for giving us his sequence distribution program and B. L. Johnson for many helpful discussions.

The Raman Spectra of Polybutadiene Rubbers

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ABSTRACT: The Raman spectra of *cis*-1,4-, *trans*-1,4-, and 1,2-polybutadiene are presented. Analysis of the spectra of these model compounds, and the normal coordinate results, enable the Raman frequencies to be classified by configurational structure type. The Raman carbon–carbon double bond stretching vibrations can be used to describe uniquely the structure content in polybutadienes.

Polymerization of 1,3-butadiene produces either 1,4 addition or 1,2 addition products, as shown in Figure 1. The 1,4 addition forms either the *cis* or the *trans* isomer, while the 1,2 addition proceeds either isotactically or syndiotactically.

From the symmetry of the repeat unit and vibrational theory one can predict both the number and spectral activity of fundamental vibrations. In general, there will be more Raman active fundamentals than are infrared active modes. If the molecule possesses a center of symmetry, the fundamentals are only Raman active or only infrared active, but are not active in both.

The normal coordinate analysis for *trans*-1,4-polybutadiene[1] and syndiotactic 1,2-polybutadiene[2] have been reported, but no analysis has been reported for either *cis*-1,4-polybutadiene or isotactic 1,2-polybutadiene. Since *trans*-1,4-polybutadiene contains a center of symmetry, all of the Raman frequencies will be mutually exclusive from the infrared frequencies. Syndiotactic 1,2-polybutadiene has C_{2v} symmetry for two chemical units in the repeating cell, which generates four symmetry species; three of these are infrared active, but all four are Raman active. *cis*-1,4-Polybutadiene has only C_s symmetry in the rubbery state and all modes are active in both Raman and infrared. Isotactic 1,2-polybutadiene has a vertical plane between chemical repeat units, perpendicular to the chain axis, to produce C_s symmetry, which has both infrared and Raman activity for all the fundamental vibrations. Raman scattering supplies new vibrational information for the models with C_i and C_{2v} which cannot be obtained by infrared measurements.

Since the properties of butadiene rubbers are linked to the amount of each structural component, it is essential to characterize multicomponent, commercial butadiene rubbers in terms of each structural component. Infrared methods for determining the unsaturation distribution have been developed.[3] However, the symmetrical carbon–carbon double bond stretching vibration, ν(C=C), in *trans*-1,4-polybutadiene is infrared inactive, so the out-of-plane hydrogen deformation vibrations are employed. This analysis[3] requires one to account for the absorption of all three structures at each of the three analytical frequencies. Extinction coefficient ratios can be determined using a matrix expression, and an unsaturation distribution can be calculated. Since the ν(C=C) vibration is Raman active for all three structural species, a determination based on the Raman ν(C=C) vibration should be possible.

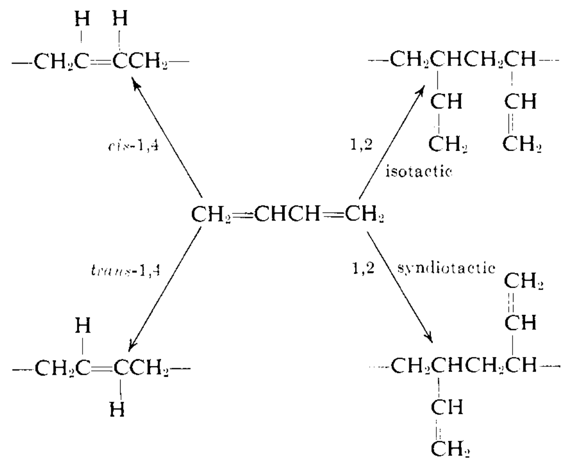

Figure 1. Polybutadiene polymerization routes.

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(1) N. Neto and C. diLauro, *Eur. Polym. J.*, 3, 645 (1967).

(2) G. Zerbi and M. Gussoni, *Spectrochim. Acta*, **22**, 2111 (1966).

(3) R. J. Silas J. Yates, and V. Thornton, *Anal. Chem.*, **31**, 529 (1959).

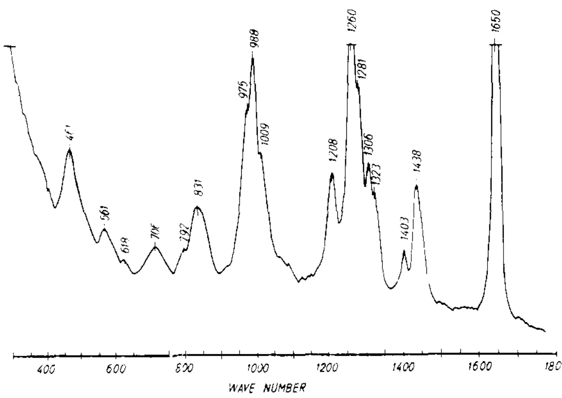

Figure 2. Raman spectrum of *cis*-1, 4-polybutadiene.

Stereospecific catalyst systems enable the polymerization of polybutadienes composed of specific structures. Using these systems as model compounds, Binder[4] re-evaluated the infrared data on butadiene rubbers.

It is the purpose of this paper to present the Raman spectra of several polybutadienes. We shall examine the spectra of *cis*-1,4-, *trans*-1,4-, and 1,2-polybutadienes, and use them as model compounds for assigning vibrations characteristic of each configurational structure type, with the aid of the vibrational analysis and infrared results. We shall follow the behavior of these bands as the structural content changes in the nonstereospecific rubbers, and we shall demonstrate that the ν(C=C) band, in particular, can be used to follow changes in configurational structure type produced by different polymerization systems.

Experimental Section

The samples used in this investigation are *cis*-1,4-polybutadiene, *trans*-1,4-polybutadiene, 1,2-polybutadiene, emulsion polybutadiene, liquid polybutadiene, lithium polybutadiene, sodium polybutadiene, and 1,2-polybutadiene. The *cis*-1,4-polybutadiene is Goodrich–Gulf CB-220; the *trans*-1,4-polybutadiene is from the Phillips Petroleum Co.; and the emulsion polybutadiene is from the B. F. Goodrich Co. All of these are commercial rubbers. The liquid polybutadiene and lithium polybutadiene were obtained from B. F. Goodrich as special preparations. The sodium polybutadiene was obtained from Goodrich–Gulf as a special preparation. The 1,2-polybutadiene was obtained from Binder and is the sample he used previously.[4] The *cis*-1,4-polybutadiene and lithium polybutadiene are clear solids. A fresh sample was cut from each of the rubber blocks, so as to expose fresh, unoxidized surfaces. These samples were nominally 3/16 in. thick and were examined by the front surface scattering technique. The liquid polybutadiene was examined using standard liquid or solution techniques. The 1,2-polybutadiene was received as a white reprecipitated powder, and was examined using a standard powder technique. The as-received *trans*-1,4-polybutadiene and sodium polybutadiene were colored and did not initially produce good spectra, so solutions were prepared in hexane and films cast onto glass slides. These solvent cast films were examined by the front surface scattering technique and gave good spectra.

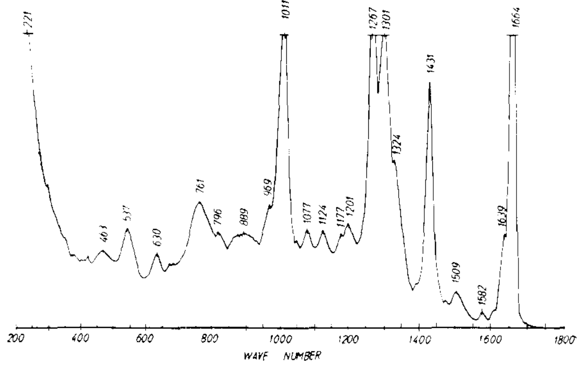

Figure 3. Raman spectrum of *trans*-1,4-polybutadiene.

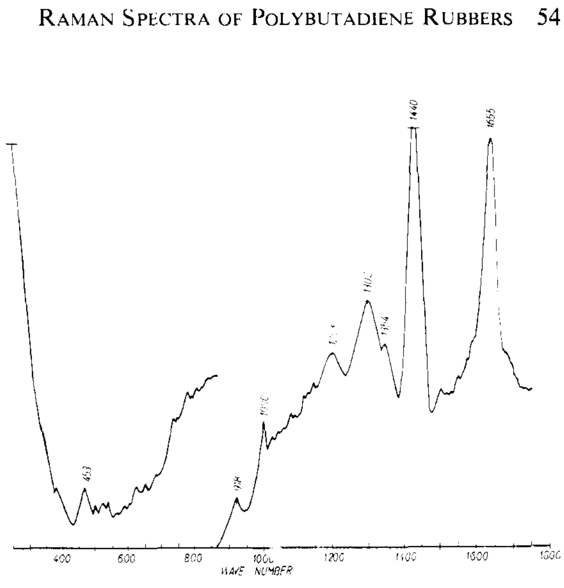

Figure 4. Raman spectrum of 1,2-polybutadiene.

The laser-excited Raman spectrometer used for this investigation has been described previously.[5] The instrument has an argon ion laser source, a Spex 1400 monochromator, and sample illuminator, an EMI 6256S photomultiplier tube, a Keithley 104 wide-band amplifier and an ac diode ring multiplier, and a Texas Instruments servoriter II chart recorder. For these experiments an RCA Model LD-2101 argon ion laser was used as the source, employing the 4880-Å exciting line.

Front surface scattering was accomplished using the opaque sample kinematic stage in the Spex sample illuminator. It inclines the sample 60° from the horizontal and focuses the beam onto the front surface of the sample. Liquid transmission sampling was performed using the liquid sample kinematic stage with a small 14-mm diameter tube replacing the liquid sample cell. The powder sampling was accomplished in an indentation in an aluminum block modeled after the opaque sampler. The surface of the block is inclined 10° from the beam, and the beam is focused on the sample.

Results

The Raman spectra of the different polybutadiene rubbers are shown in Figures 2–4. A tabulation of the frequencies from these spectra is shown in Table I, as well as both the high-frequency values, not shown in the figures, and assignments based on normal coordinate analysis calculations[1,2] and Binder's infrared analysis.[4]

cis-1,4-Polybutadiene produces a very strong, good-quality spectrum, shown in Figure 2. There are three low frequency bands at 126, 155, and 237 cm^{-3}, which

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(4) J. L. Binder, *J. Polym. Sci., Part A-1*, **47** (1963).

(5) S. W. Cornell and J. L. Koenig, *J. Appl. Phys.*, **39**, 4883 (1968).

Table I
Polybutadiene Raman Frequencies[a]

Wave number, cm^{-1}			
cis-1,4	*trans*-1,4	1,2	Assignment
		3085[b]	$\nu_{a}(\mathrm{CH_2{=}CH})_{0}$ 1,2
3006	3003	3007[b]	$\nu(\mathrm{CH{=}CH})$ *cis*
	2932	2927[b]	$\nu_{s}(\mathrm{CH_2{=}CH})i$ 1,2
2896	2898	2905[b]	$\nu(\mathrm{CH{=}CH})$ *trans*
	2878		ν_{a}
2850	2846	2856[b]	ν_{s}
1650	1664	1655	$\nu(\mathrm{C{=}C})$ *cis*, *trans*, vinyl
	1639	1643	$\nu(\mathrm{C{=}C})$ vinyl
1438	1431	1440	$\delta(\mathrm{CH_2})$
1403		(1416)	$\delta(\mathrm{{=}CH})_{ip}$
1323	1324	1354	$\gamma_{w}(\mathrm{CH_2})$
1306	1301	1304	$\delta(\mathrm{{=}CH})_{ip}$
1287			
1260	1267	(1268)	$\gamma_{t}(\mathrm{CH_2})$
1208	1201	1203	
	1177		
	1124		$\nu_{s}(\mathrm{C{-}C})$ *trans*
	1077		
1009	1011		$\nu_{a}(\mathrm{C{-}C})$
		1000	$\gamma_{w}(\mathrm{{=}CH})_{op}$ 1,2
988			
975	969		$\gamma_{w}(\mathrm{{=}CH})_{op}$ 1,4
		(910)	$\delta(\mathrm{{=}CH_2})_{op}$ 1,2
	889?		
831	837?		
792	796		
	761		$\gamma_{r}(\mathrm{CH_2})$ *trans*
706			
618	630		
561	537	(547)	$\delta(\mathrm{CCC})$
461	463	453	$\delta(\mathrm{C{=}C{-}C})$
237	221	215	$\tau(\mathrm{C{-}C})$
155			
126			

[a] ( ) = sodium polybutadiene; ν = stretch, γ = bend, δ = deformation, τ = torsion; a = asymmetric, s = symmetric, w = wag, t = twist, r = rack; ip = in plane, op = out of plane, i = phase in, o = out of phase. [b] See ref 3.

are not shown in Figure 2. The *trans*-1,4-polybutadiene spectrum, shown in Figure 3, was produced from a film cast from hexane solution. In some places the background level is high; specifically, the exact position of the broad band at 889 cm^{-1} is questionable.

The spectrum of the 1,2-polybutadiene sample obtained from Binder is shown in Figure 4. This powder sample did not produce spectrum of the same quality as the other butadiene rubber spectra. The bands from 1200 to 1700 cm^{-1} are clear, but the remainder of the spectrum has a very high background level. Detailed scanning of the ν(C=C) region showed a very badly overlapped shoulder on the 1655-cm^{-1} band appearing at 1643 cm^{-1}. The appearance of the ν(C=C) at 1655 cm^{-1} is anomalous, as this band appears at 1639 cm^{-1} in all of the other rubber samples. All other attempts to obtain the spectrum in a fashion similar to the other rubber samples met with failure. A film cast from hexane solution, which was highly crystalline and crumbled easily, did not yield a good spectrum either. Consequently, the experimental results for 1,2-polybutadiene are the least reliable. In the discussion Zerbi and Gussoni's normal coordinate results[2] are relied upon heavily, because of our concern about the experimental results.

Discussion

The model systems for butadiene rubber are *cis*-1,4-polybutadiene, *trans*-1,4-polybutadiene, and 1,2-polybutadiene. After closely examining these systems, we should be able to assign bands to the different configurational structural types. Fortunately, the normal coordinate analysis for *trans*-1,4-polybutadiene and syndiotactic 1,2-polybutadiene have been reported. The results of Neto and diLauro[1] on *trans*-1,4-polybutadiene are shown in Table II with our Raman data for the A_g modes, which are infrared inactive. Their calculated results show good agreement with the observed infrared and Raman frequencies.

The normal coordinate results of Zerbi and Gussoni[2] for syndiotactic 1,2-polybutadiene shown in Table III are in good agreement with the Raman frequencies for the A_2 modes, which are infrared inactive. No one to date has reported the vibrational analysis of *cis*-1,4-polybutadiene. The computer memory storage requirements are extremely large for a molecule having 20 atoms and no local symmetry, and are beyond the reach of most computers. Since the stereospecific *cis*-1,4-polybutadiene rubber is very high in *cis* content (98%), we can safely use the experimentally observed frequency values to determine *cis*-structure placements. Binder's[4] infrared assignments are used as the basis for making Raman band assignments in *cis*-1,4-polybutadiene.

Thus in *trans*-1,4-polybutadiene Raman spectroscopy provides new information which cannot be obtained by infrared analysis alone, since the A_g modes are infrared inactive under C_i symmetry. Likewise, the C_{2v} symmetry present in syndiotactic 1,2-polybutadiene requires all fundamental vibrations to be Raman active, but only three-fourths of the groups are infrared active. For these two species the Raman data are necessary before a complete analysis can be made.

The Raman spectra for *cis*-1,4-polybutadiene, *trans*-1,4-polybutadiene, and 1,2-polybutadiene, respectively, are shown in Figures 2, 3, and 4. The normal coordinate analyses predict ν(C=C) vibrations occurring at 1667 and 1642 cm^{-1}, respectively, for *trans* and 1,2 placements. The Raman spectra indicate these vibrations occurring at 1650, 1664, and 1655 cm^{-1}, respectively, for *cis*, *trans*, and 1,2 placements. However, all other butadiene rubber containing vinyl 1,2 placements indicate the ν(C=C) vibration occurring at 1639 cm^{-1}. When the spectrum of 1,2-polybutadiene was rerun at high-resolution conditions, a very badly overlapped shoulder appeared at 1643 cm^{-1}, in addition to the strong 1655-cm^{-1} band; it is characteristic of "isolated" 1,2-vinyl placements. Perhaps the 1655-cm^{-1} band is characteristic of "coupled or ordered" 1,2 placements. Thus the ν(C=C) vibration can be used to characterize polybutadienes by configurational structure type using the 1650-cm^{-1} band characteristic of *cis* content, the 1664-cm^{-1} band characteristic of *trans* content, and the 1639- (and 1655-) cm^{-1} bands characteristic of 1,2-vinyl content.

The CH stretching vibrations of the carbon–carbon double bond cannot be used easily to determine configurational structure. There is a band predicted[1] at

TABLE II
NORMAL COORDINATE ANALYSIS FREQUENCIES OF *trans*-1,4-POLYBUTADIENE[a]

	Obsd	Calcd	Diff	Assignment[b]
A_g	3003	3272	24	ν_{HD} (98)
	2932	2923	−9	ν_{HC} (98)
	2846	2848	2	ν_{HC} (99)
	1664	1667	3	ν_{D} (76), ν_{C} (15)
	1431	1433	2	γ_{H} (77)
	1324	1331	7	γ_{HC} (43), $\gamma_{\mathrm{HC'}}$ (26)
	1301	1304	3	γ_{HC} (56), $\gamma_{\mathrm{HC'}}$ (25)
	1267	1259	−8	γ_{HD} (29), ν_{C} (17), $\gamma_{\mathrm{HC'}}$ (16), γ_{HC} (16)
	1124	1141	17	ν_{C} (31), $\gamma_{\mathrm{HC'}}$ (27), γ_{CD} (16)
	1011	1039	28	γ_{C} (79)
	969	962	−7	$\gamma_{\mathrm{HC'}}$ (39), ν_{C} (17)
	761	759	−2	δ_{H} (66), $\gamma_{\mathrm{HC'}}$ (13)
	537	555	18	γ_{C} (32), γ_{CD} (31), γ_{HC} (17), $\gamma_{\mathrm{HD'}}$ (16)
	221	223	2	τ_{CD} (57), ν_{C} (17)
A_u	3018	3009	−9	ν_{HD} (99)
	2915	2914	−1	ν_{HC} (99)
	2840	2842	2	ν_{HC} (100)
	1453	1426	−27	γ_{H} (80), $\gamma_{\mathrm{HC'}}$ (14)
	1312	1302	−10	$\gamma_{\mathrm{HC'}}$ (36), $\gamma_{\mathrm{HD'}}$ (22), γ_{HC} (20), γ_{HD} (16)
	1235	1245	10	$\gamma_{\mathrm{HC'}}$ (53), γ_{HC} (43)
	1075	1066	−9	ν_{C} ((37), $\gamma_{\mathrm{HC'}}$ (25), γ_{HD} (21), γ_{HC} (21)
	1054	1035	−19	ν_{C} (58)
	978	986	8	τ_{D} (59), δ_{H} (32)
	773	769	−4	γ_{HC} (74), $\gamma_{\mathrm{HC'}}$ (22)
	440	426	−14	γ_{C} (56), γ_{HC} (13), δ_{H} (13)
		301		γ_{CD} (52), τC (16), γHD (13)

[a] ν = stretch, γ = bend, δ = deformation, τ = torsion; $\nu_{\mathrm{HD}} = \nu(\text{=CH})$, $\nu_{\mathrm{HC}} = \nu(\text{-CH})$, $\nu_{\mathrm{D}} = \nu(\text{C=C})$, $\nu_{\mathrm{C}} = \nu(\text{CC})$, $\gamma_{\mathrm{C}} = \gamma(\text{CCC})$, $\gamma_{\mathrm{CD}} = \gamma(\text{C=CC})$, $\gamma_{\mathrm{H}} = \gamma(\text{HCH})$, $\gamma_{\mathrm{HD}} = \gamma(\text{HC=C})$, $\gamma_{\mathrm{HD'}} = \gamma(\text{CHC=})$, $\gamma_{\mathrm{HC}} = \gamma(\text{HCC-})$, $\gamma_{\mathrm{HD'}} = \gamma(\text{HCC=})$, $\delta_{\mathrm{H}} =$ HC(=C)C), D = (-C=C-), C = (-CC-), CD = (=CC-). [b] See ref 2.

2923 cm^{-1} characteristic of the *trans* placement. Infrared results[4] indicate a band at 3012 cm^{-1} characteristic of the *cis* placement. These bands are observed in Raman spectrum at 2932 cm^{-1} (2922 cm^{-1} in emulsion polybutadiene) and 3006 cm^{-1}, respectively. The band characteristic of vinyl placement is predicted[2] at 3085 cm^{-1} and observed at 3080[7] or 3077 cm^{-1} [4] in the infrared spectrum and 3074 cm^{-1} in the Raman spectrum. There is, however, the symmetric CH stretching mode of the ($CH=CH_2$) unit which occurs at 3012 cm^{-1} [2,6] coincident with the CH stretching mode of the *cis* (CH=CH) unit. Because of this superposition, the CH stretching frequencies cannot be used for structure determination.

The hydrogen out-of-plane vibrations used for structure determination by Silas[3] are the 741-, 971-, and 909-cm^{-1} bands for *cis*-1,4, *trans*-1,4, and vinyl content, respectively. Other infrared peaks for the *cis*-1,4 structure at 690 and 775 cm^{-1} must also be considered in the *cis* determination. The 971-cm^{-1} infrared band calculated at 986 cm^{-1} also has a very high torsional component, in addition to the out-of-plane motion.[1] The 909-cm^{-1} infrared band calculated to 907 cm^{-1} [2] is assigned to rocking, $\nu_r(CH_2)$, mode, and has also been assigned to Binder[5] to CH_2 out-of-plane motion of the ($CH_2=CH$) group. In the Raman spectra bands occur at 706, 969, and 910 cm^{-1} respectively, for *cis*, *trans*, and vinyl. These bands are not particularly strong in the Raman spectra and would not make good analytical bands. In addition, the 969-cm^{-1} band has scattering bands occurring with +8 cm^{-1} in all the spectra, except 1,2, and so is indicative of total 1,4 placements rather than *trans*-1,4 placements.

Utilizing the model compound spectra and the normal coordinate analyses, the Raman scattering bands can be classified according to type of configuration structure. This compilation is shown in Table IV.

Examination of the Raman spectra has shown that the Raman active ν(C=C) vibrations can be used to follow changes in structure content. In principle, a quantitative measure of these configurational structures could be obtained by resolving the three peaks. Scans for the six butadiene rubber samples obtained with the instrument operating under high resolution conditions are shown in Figure 5. The three bands are resolved at the proper frequency positions. Band overlap is evidenced if either the *cis* band is strong and the *trans* band weak or conversely. In cases where nearly equal amounts of structure occur, the peak resolution is improved.

Silas[3] presented a calculational method for determination of extinction coefficient ratios in multicomponent systems. For the purposes of this paper, such detailed calculations will not be attempted for the Raman results. Because the vibrations are all in the same spectral region and due to similar motions, as a first approximation, we shall assume that the extinction coefficients ratios do not deviate appreciably from a fixed value, so simple peak height ratios or area ratios will be used to estimate structure content. Using this scheme, tentative structure content characterization can be made.

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(6) D. Morero, E. Mantica, and L. Porri, *Nuovo Cimento Suppl.*, **15**, 136 (1960).

Table III

Normal Coordinate Analysis Frequencies of Syndiotactic 1,2-Polybutadiene[a,b]

	Obsd	Calcd	Diff	Assignment
A_1	3080	3085	5	$\nu(=CH_2)$
		3047		$\nu(=CH)$
	3012	3007	−5	$\nu(=CH_2)$
	2913	2905	−8	$\nu(-CH)$
	2847	2856	9	$\nu(CH_2)$
	1643	1642	−1	$\nu(C=C)$ (86)
	1452	1457	5	$\delta_i(CH_2)$ (90)
	1419	1424	5	$\delta_i(=CH)$ (44), $\delta_i(=CH_2)$ (44)
	1333	1329	−4	$\delta_i(=CH)$ (50)
	1265)	1258	−7	$\gamma_{to}(CH_2)$ (41)
	(1203)	1205	2	$\delta_i(CH)$ (40)
	1131	1131	0	$\nu(CC)$ (42), $\delta_i(CH)$ (37)
	1045	1054	9	$\delta_i(=CH)$ (43), $\gamma_{to}(CH_2)$ (35)
	815	814	−1	$\nu(=CC)$ (57), $\gamma_{ro}(CH_2)$ (30)
	(469)	470	1	$\delta_i(C=C\text{-}C)$ (35)
		321		$\gamma_{ro}(=CH_2)$ (39), $\delta(C=C\text{-}C)$ (34)
A_2	2847	2855	8	$\nu(CH_2)$
	(1440)	1447	7	$\delta_i(CH_2)$ (75)
	(1434)	1433	−1	$\gamma_{ti}(CH_2)$ (46)
	1131	1131	0	$\gamma_{ti}(=CH_2)$ (61)
	(1079)	1074	−5	$\nu(CC)$ (84)
	(997)	984	−13	$\gamma_{wo}(=CH_2)$ (90)
	(910)	897	−13	$\gamma_{ti}(CH_2)$ (95)
	(680)	679	−1	$\gamma_{wo}(=CH)$ (33)
		516		$\delta(CCC)$ (47)
		197		$\delta(CCC)$ (41)
B_1		2927		$\nu(CH_2)$
	1343	1332	−11	$\gamma_{wi}(CH)$ (63)
	1213	1200	−13	$\gamma_{wi}(CH_2)$ (62)
		1131		$\gamma_{to}(=CH_2)$ (60), $\gamma_{wi}(=CH)$ (34)
	1070	1076	6	$\gamma_{wi}(CH_2)$ (57)
	991	985	−6	$\gamma_{wi}(=CH_2)$ (92)
	908	907	−1	$\gamma_{ro}(CH_2)$ (63)
	664	664	0	$\gamma_{wi}(=CH)$ (50), $\gamma_{to}(=CH_2)$ (27)
		349		$\delta(CCC)$ (73)
B_2	3080	3085	5	$\nu(=CH_2)$
		3047		$\nu(=CH)$
	3012	3007	−5	$\nu(=CH_2)$
	2913	2927	14	$\nu(CH_2)$
		2902		$\nu(CH)$
	1643	1642	−1	$\nu(C=C)$ (86)
	1419	1424	5	$\delta_o(=CH_2)$ (88)
	1333	1334	1	$\delta_o(CH)$ (31)
	1294	1290	−4	Mixing
		1194		$\nu(C\text{-}C=)$ (32)
		1117		$\gamma_{wo}(CH_2)$ (72)
		1085		$\nu(CC)$(64)
		1021		$\gamma_{ro}(=CH_2)$ (45)
	788	790	2	$\nu(C\text{-}C=)$ (52)
		579		δ $(CCC=)$ (36), δ $(C=C\text{-}C)$ (27)
		356		$\delta(CCC)$ (57)
		295		Skeletal deformation

[a] See ref 3. [b] ( ), Raman data.

The structural composition of all the rubbers, except 1,2-butadiene, is shown in Table V. The first column shows the calculation based on peak heights. The second column shows infrared results for these rubbers. Only the liquid polybutadiene infrared results were run on the same sample. All the other infrared values are typical data, not results for these specific samples. The infrared results for polybutadienes agree well with the nmr results and are, now generally accepted, as indicative of the unsaturation distribution. In all cases, the general trend observed using the Raman $\nu(C=C)$vibrations, without using involved calculational corrections, or properly calibrating the scattering coefficients, is consistent with the infrared calculations. Further improvement can be made by careful calibration of the scattering coefficients for each band. Only the emulsion polybutadiene Raman results are inconsistent with the infrared results. Both methods indicate high *trans* content, but the Raman results suggest that the residual unsaturation, the *cis* content is slightly higher than the

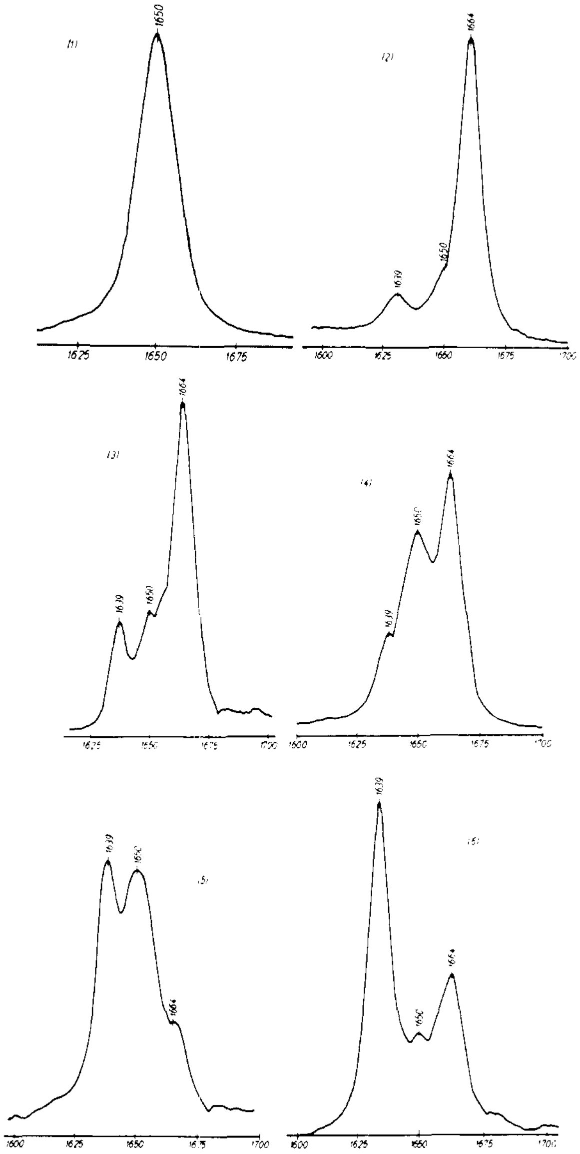

Figure 5. High-resolution scan of ν (C=C) region in butadiene rubbers: (1) *cis*-1,4-polybutadiene, (2) *trans*-1,4-polybutadiene, (3) emulsion polybutadiene, (4) lithium polybutadiene, (5) liquid polybutadiene, (6) sodium polybutadiene.

vinyl content; however, the infrared determination suggests that the vinyl content is twice as great as the *cis* content. Infrared data for *trans*-1,4-polybutadiene and sodium polybutadiene were not available, so literature values on similar material[3,7] were compared. The general nature of the agreement between infrared and Raman constitutes further evidence for the correctness of the assignment.

TABLE IV

POLYBUTADIENE FREQUENCY ASSIGNMENT BY CONFIGURATIONAL STRUCTURE TYPE

Wave number, cm^{-1}			
cis-1,4	*trans*-1,4	1,2	Assignment
		3074	ν_a(=CH)
3006	2922	2987	ν(=CH)
	2878		
1650	1664	1655	ν(C=C)
		1639	ν(C=C)
1438	1431	1440	$\delta(CH_2)$
1403		1416	$\delta_i(=CH)_{ip}$
1323	1324	1354	$\gamma_w(CH_2)$
1306	1301	1304	$\delta(=CH)_{ip}$
1287			
1260	1267	1268	$\gamma_t(CH_2)$
	1124		
975	969	1000	$\gamma_{wo}(=CH_2)$
		910	$\delta(=CH_2)$
561	537		δ(CCC)
237	221	215	τ(CC)

TABLE V

STRUCTURE CONTENT OF POLYBUTADIENES

	Peak heights, %			Ir values,[c] %		
Polybutadiene	*cis*	*trans*	Vinyl	*cis*	*trans*	Vinyl
cis-1,4-PBD	100			99		
trans-1,4-PBD	17	73	10	9[a]	89	2
Emulsion PBD	21	59	20	11	68	21
Liquid PBD	41	16	43	52	13	35
Lithium PBD	36	47	17	45	45	10
Sodium PBD	17	26	57	14[b]	26	60

[a] Typical data; see ref 3. [b] Data of Roha; see ref 7. [c] Determined by B. F. Goodrich Co. and Goodrich-Gulf Chem. Inc.

In conclusion, we have described the Raman spectra of several polybutadienes and compared the results with infrared measurements and normal coordinate analysis predictions. We have demonstrated the possibility of using the ν(C=C) vibrational modes for determining structure type in polybutadienes.

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(7) M. Roha, *Fortschr. Hochpolym. Forsch*, 1, 512 (1960).