Raman Spectra of Polyisoprene Rubbers

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ABSTRACT: The Raman spectra of *cis*-1,4-, *trans*-1,4-, and 3,4-polyisoprene are presented, and the frequencies are classified by configurational structure type. The stretching frequency of the carbon–carbon double bond vibrations are used to describe structure content. Only Raman bands characteristic of total 1,4 content and total vinyl content can be observed. Tentative values of structure content determined by both peak height and peak area are presented for two mixed structure rubbers.

The polymerization of 1,3-polyisoprene can proceed by either 1,4 addition or vinyl addition. In the former case, either the *cis* or the *trans* isomer can occur. Thus, four structural units are possible: *cis*-1,4, *trans*-1,4, 3,4-vinyl, and 1,2-vinyl. The 1,2-vinyl unit is identical with the 1,2-polybutadiene vinyl unit. Figure 1 shows these four possible structures arising from the different polymerization routes.[1]

Infrared analysis of polyisoprenes has shown absorbance bands at 1130 and 1150 cm^{-1} characteristic of *cis*-1,4 and *trans*-1,4 placements, respectively.[2] A unique band at 1140 cm^{-1} has been observed[3] for 3,4-polyisoprene. The band at 910 cm^{1-}, observed in polybutadienes, is characteristic of 1,3 placement.[4] Using these bands, structural determinations can be made on isoprene rubbers. However, the results for isoprene rubbers have not been consistent with nmr results, in contrast to polybutadiene for which infrared measurements yield acceptable results and are in good agreement with nmr results. Kossler and Vodehnal[3] assert that only long sequences of *cis*- or *trans*-1,4 placements give rise to absorbance in the 1100- and 1150-cm^{-1} region. They report better results using the 572, 980, and 888-cm^{-1} bands for *cis*-1,4, *trans*-1,4, and vinyl 3,4, respectively.

It is the purpose of this paper to report the Raman spectra of several polyisoprenes. No normal coordinate analyses have been reported for polyisoprenes, so we do not have this aid in assigning the Raman frequencies. Since there is no local symmetry in the isoprene chemical repeat unit, no selection rules due to symmetry occur; the infrared assignments can be used to assign bands in the Raman spectrum. We have demonstrated the sensitivity of the stretching mode of the carbon–carbon double band, ν(C=C) vibration in the Raman spectra of polybutadienes for determining structure content.[5] We shall investigate the behavior of these motions in polyisoprenes. From the Raman spectral frequencies, we shall classify the observed bands for configurational structure type.

Experimental Section

The samples used in this investigation are *cis*-1,4-polyisoprene, *trans*-1,4-polyisoprene, cobalt polyisoprene, sodium polyisoprene, and 3,4-polyisoprene. The *cis*-1,4-polyisoprene is Goodrich–Gulf SN-900, and the *trans*-1,4-polyisoprene is from the Polymer Corp. The cobalt and sodium polyisoprenes were specially prepared by J. White at Goodrich–Gulf Chemical Inc. The 3,4-polyiosprene was obtained from Binder and is the sample he used previously.[6] The *cis*-1,4-polyisoprene is a clear solid. A fresh sample was cut from the rubber slab so as to expose fresh unoxidized surfaces. The sample was nominally $^{3}/_{16}$ in. thick and was examined by front surface scattering. The *trans*-1,4-polyisoprene (as received) did not give a good spectrum. A film cast from hexane solution onto a glass slide produced a sample which gave a good spectrum by front surface scattering. Both the cobalt and sodium polyisoprenes are colorless; samples of about $^{1}/_{8}$ in. thickness were placed on glass slides and examined by front surface scattering. The 3,4-polyiosprene sample was received as a white reprecipitated powder, and was examined by the powder sampling technique.

The laser-Raman spectrometer used for this investigation has been described previously.[7] It consists of an RCA Model LD-2101 argon ion laser, a Spex 1400 monochromator with sample illuminator attachment, 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.

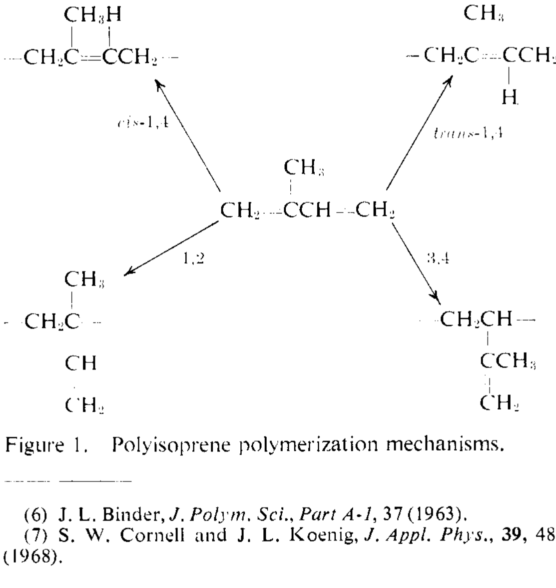

Figure 1. Polyisoprene polymerization mechanisms.

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[1] J. E. Field, D. E. Woodford, and S. D. Gehman, *J. Appl. Phys.*, **17**, 386 (1946).

[2] M. A. Golub, *J. Polym. Sci.*, **36**, 523 (1959).

[3] I. Kossler and J. Vodehnal, *J. Polym. Sci., Part B*, **1**, 415 (1963).

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

[5] S. W. Cornell and J. K. Koenig, *Macromolecules*, **2**, 539 (1969).

[6] J. L. Binder, *J. Polym. Sci., Part A-1*, 37 (1963).

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

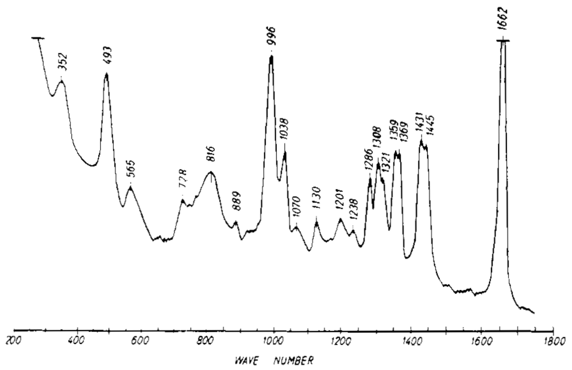

Figure 2. Raman spectrum of *cis*-1,4-polyisoprene.

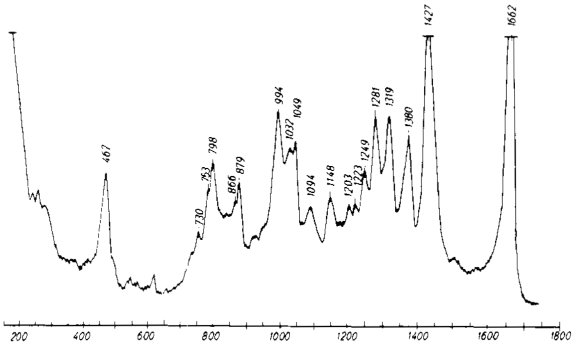

Figure 3. Raman spectrum of *trans*-1,4-polyisoprene.

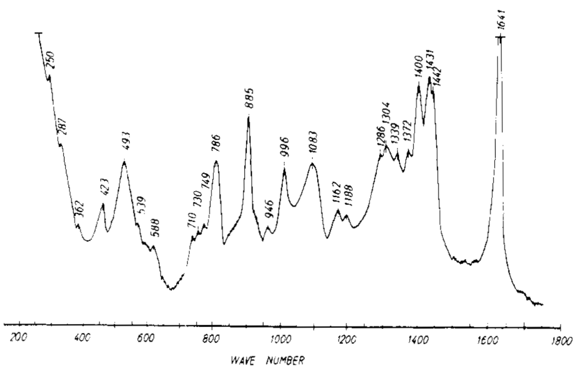

Figure 4. Raman spectrum of 3,4-polyisoprene.

Results

The Raman spectra of the isoprene rubbers are shown in Figures 2, 3, and 4. A tabulation of all the frequencies from these spectra is shown in Table I. The high-frequency region, not shown in the figures, is also included in Table I. Frequency assignments in Table I are based on the infrared assignments of Binder.[6]

The high-quality spectrum of *cis*-1,4-polyisoprene is shown in Figure 2. There are doublets appearing at 1431 and 1445, and 1359 and 1369 cm^{-1}. The ν(C=C) band appears at 1662 cm^{-1}. There is a band at 1130 cm^{-1}, as observed in the infrared spectrum.

The spectrum of *trans*-1,4-polyisoprene is shown in Figure 3. The received sample did not produce a good spectrum, but a film cast from hexane solution did produce a good spectrum. The ν(C=C) band appears at 1662 cm^{-1}, also noted for the *cis*-1,4 sample. There are no doublets in the 1350–1450-cm^{-1} region. There

TABLE I

POLYISOPRENE RAMAN FREQUENCIES[a]

Wave number, cm^{-1}				
cis- 1,4	*trans*- 1,4	3,4	1,2[b]	Assignment
		3068	3085	ν_a(=CH)(C(CH$_3$)=CH$_2$)
3033				ν(=CH)(C(CH$_3$)=CH–)
	3010		3007	
		2980		ν_s(=CH)(C(CH$_3$)=CH$_2$)
2957	2969	2964		ν_a(CH$_3$)
2929			2927	
2910		2912		ν_i(CH$_2$)
	2903	2901	2905	
2878	2879	2876		ν_s(CH$_3$)
		2861		
2853	2850		2856	
	2839			ν_o(CH$_2$)
2724	2723			
1662	1662			ν(C=C) 1,4
		1641	1643	ν(C=C) vinyl
1445		1442		δ_a(CH$_3$)
1431	1434	1431	1440	δ(CH$_2$)
			1400	
	1380			δ_s(CH$_3$)
1369			1372	
				γ_w(CH$_3$)
1359	1354		1354	γ_w(CH$_2$)
		1339		
1321	1323			δ(=CH)$_{ip}$ 1,4
1308		1304	1304	δ(=CH)$_{ip}$ 3,4
1286	1281	1286		
	1249			
1238				
	1223			
1201	1203		1203	
		1188		
			1162	ν(C–C) 3,4
	1148			ν(C–C) *trans*
1130				ν(C–C) *cis*
	1094		1083	
1070				
	1049			
1038	1032			γ_r(CH$_3$)?
996		996	1000	
		946		
889		885		γ(CH)
	879			
	866			
816				
	798			
		786		
	753	749		
728	730	730		
		710		
565		588		
			539	γ_w(=CC$_2$), δ(CCC)
493		493		γ_r(=CC$_2$), γ_s(=CC$_2$)
	467		453	
428		423		γ_r(=CC$_2$)
355		362		γ_s(=CC$_2$)
343				
		287		γ_s(=CC$_2$), δ(CCC)
		250		δ(CCC), γ_w(=CC$_2$)
179			215	

[a] ν_o = out-of-phase stretch, ν_i = in-phase stretch, ν_a = asymmetric stretch, ν_s = symmetric stretch, $\delta(\ )_{ip}$ = in-plane deformation, ν = stretch, γ_r = rock, γ_s = scissor, γ_w = wag, δ = deformation. [b] See ref 5.

is a band at 1148 cm^{-1} equivalent to the 1150-cm^{-1} band observed in the infrared spectrum.

The powder sample of 3,4-polyisoprene produced a good spectrum, shown in Figure 4. The ν(C=C) band appears at 1641 cm^{-1}. The higher frequency 1431–1442-cm^{-1} doublet is observed, but the lower frequency 1359–1369-cm^{-1} one is absent. The 1400-cm^{-1} band is stronger in this spectrum than any of the other spectra. There is a band at 1162 cm^{-1} instead of the 1140-cm^{-1} band reported for infrared. There is also a band at 1188 cm^{-1}. The 885-cm^{-1} band is very intense, and, as the infrared results for 888 cm^{-1} report,[3] may be a good analytical band for structure determination.

Discussion

The assignments for the Raman bands reported in Table I were taken from Binder's infrared assignments.[6] The region below 550 cm^{-1} was assigned using Shimanouchi and Abe's skeletal deformation vibrations analysis.[8] Examination of the spectra for the *cis*-1,4, *trans*-1,4, and 3,4-polyisoprenes allows compilation of frequencies by configurational structure type. These results are tabulated in Table II.

TABLE II
POLYISOPRENE FREQUENCY ASSIGNMENT BY CONFIGURATIONAL STRUCTURE TYPE

Wave number, cm^{-1}				
cis-1,4	*trans*-1,4	1,2	3,4	Assignment
3033	3010	3074	3068	$\nu(=\text{CH})$
		2987	2980	$\nu_s(=\text{CH})$
1662	1662	1639	1641	$\nu(\text{C}=\text{C})$
1445	1445	(1440)	1442	$\delta_a(\text{CH}_3)$
1369	1380		1362	$\delta_s(\text{CH}_3)$
1321	1323			$\delta(=\text{CH})_{ip}$?
1308		1304	1304	$\delta(=\text{CH})_{ip}$?
1130	1148	(1131)	1162	$\nu(\text{C–CH}_3)$
1070	1094		1083	?
		910		$\gamma_r(\text{CH}_2)$
889	879		885	$\delta(\text{CH})$
565			588	?

In the high-frequency region, there appear four distinct bands at 3033, 3010, 3074, and 3078 cm^{-3}, respectively, for *cis*- and *trans*-1,2 and 3,4 placements. The problem of overlap of a vinyl peak with the *cis* peak, encountered with polybutadienes, does not appear to occur for polyisoprenes. Although the ν(=CH) vibrations show a different frequency for each structure, they are badly overlapped by the ν(CH$_2$) vibrations and so are not useful as analytical bands for structure determination.

The ν(C=C) band occurs at 1662 cm^{-1} for both *cis*- and *trans*-1,4 placements. This peak was noted at 1664 cm^{-1} in polybutadiene for *trans*-1,4 placement. The 3,4-vinyl position is located at 1641 cm^{-1}. For 1,2 placements in polybutadienes it was observed at 1639 cm^{-1}. There appears to be little if any difference in the location of the ν(C=C) band for 1,2 and 3,4 placements. For isoprenes we are able to detect only total 1,4 placements and total vinyl placements, in contrast to polybutadienes where a different band position was observed in the ν(C=C) frequency region for each structured type.

The δ(CH$_3$) vibrations have different band positions for each structure type, but the separation is so slight that distinct peaks would be difficult to resolve in a mixture of these structures. The same phenomena, which was observed for the ν(C=C) vibration, is noted for the δ(=CH)$_{ip}$ vibration. *cis* and *trans* content are observed at 1321 and 1323 cm^{-1}, respectively. The positions for 1,2 and 3,4 vinyl are both at 1304 cm^{-1}. However, there is also a band in the *cis* spectrum, appearing at 1308 cm^{-1}, which could create problems for quantitative structure determination.

The bands in the 1130–1150-cm^{-1} region, suggested by Kossler and Vodehnal[3] to describe long-range order, appear at 1130, 1148, and 1162 cm^{-1}, respectively, for *cis*, *trans*, and 3,4 placements. Zerbi and Gussoni[9] predict a band at 1131 cm^{-1} for 1,2-polybutadiene, but no such peak was observed in the spectrum of sodium polybutadiene. If present, this peak would affect *cis*-content results. In the Raman spectra, these bands are weak and would not make good analytical bands for structure determination.

There are weak bands in the 1070–1100-cm^{-1} region of the Raman spectrum which show a sufficient separation in position among structure types. These appear at 1070, 1094, and 1083 cm^{-1} for *cis*, *trans*, and 3,4 placements.

The 910-cm^{-1} band in the 1,2-polybutadiene spectrum can be used to determine 1,2-vinyl content. The ir band at 888 cm^{-1} appearing at 855 cm^{-1} was suggested for measuring 3,4 content.[3] This appears to be a good suggestion as the 885-cm^{-1} band is moderately strong in the 3,4 spectrum, and appears in both the cobalt and sodium polyisoprene spectra. However, there is a very weak band at 889 cm^{-1} in the *cis* spectrum and medium band at 879 cm^{-1} in the *trans* spectrum which may cause some interference. The 572-cm^{-1} band was suggested for measuring *cis* content.[3] There is a band at 565 cm^{-1} in the *cis* spectrum, and also a band at 588 cm^{-1} in the 3,4 spectrum. Since these are broad bands of weak intensity, overlap may be a problem, but otherwise the suggestion is feasible. The suggestion of using the 980-cm^{-1} band for *trans* content[3] has some difficulties. Bands are observed at 996, 994 and 996 cm^{-1}, respectively, for the *cis*, *trans*, and 3,4 spectra. No band at 980 cm^{-1} is observed.

The results of this examination are that no unique, strong bands exist in the Raman spectrum for measuring structural placements as was found for polybutadienes. However, total 1,4 and vinyl content can be measured using the ν(C=C) bands at 1662 and 1641 cm^{-1}. A high-resolution scan of this region, shown in Figure 5, was made, as was done for the polybutadienes, and the structure content reported in a similar manner.[5] Both peak height and peak areas of the band were measured. The *cis*-1,4- and *trans*-1,4-polyisoprenes both produced a single peak at 1662 cm^{-1}. The 3,4-polyisoprene produced a single peak at 1641, although some noise was present at 1662 cm^{-1}. The results for the cobalt and sodium isoprenes are reported in Table **III**.

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(8) T. Shimanouchi and Y. Abe, *J. Polym. Sci., Part A-2*, **6**, 1419 (1968).

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

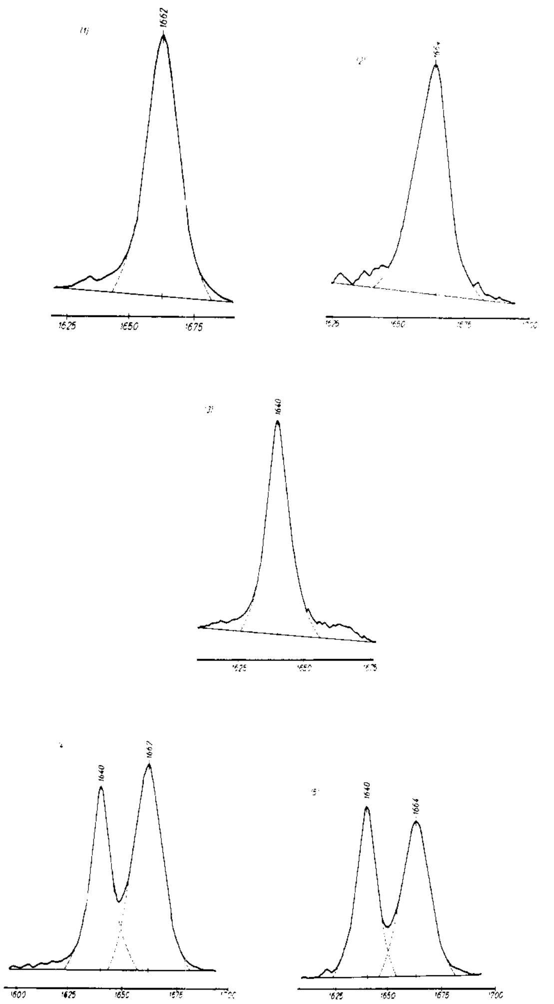

Figure 5. High-resolution scan of ν(C=C) region in isoprene rubbers: (1) *cis*-1,4-polyisoprene, *trans*-1,4-polyisoprene, (3) 3,4-polyisoprene, (4) cobalt polyisoprene, (5) sodium polyisoprene.

Because the 1662-cm^{-1} peak is broader than the 1641-cm^{-1} peak, the results based on peak area show a higher 1,4 content than the results based on peak height. No infrared or nmr analysis is currently available for these special preparations, so detailed comparison cannot be made. Some data on sodium isoprene were presented by Sterns and Forman,[10] also shown in Table III. Adding up 1,4 and vinyl content for their values indicates a better agreement with the peak height determination than the peak area determination.

TABLE III
STRUCTURE CONTENT OF POLYISOPRENES

Measurement	% structure	Cobalt	Sodium
Peak height	1,4	53	48
	Vinyl	47	52
Peak areas	1,4	61	56
	Vinyl	39	44
Lit. values[a]	*cis*-1,4		0
	trans-1,4		43
	1,2-Vinyl		6
	3,4-Vinyl		51

[a] Data of Sterns and Forman.[10]

In conclusion, only 1,4 and vinyl content for polyisoprenes can be determined by Raman spectroscopy. Values for *cis*- and *trans*-1,4 content must be determined by a ratio of two bands characteristic of *cis* and *trans* content, respectively, and the value for total 1,4 content. The 565-cm^{-1} band might be a proper choice for the *cis* band, but no comparable band (996 cm^{-1}) is available for the *trans* band. The 885-cm^{-1} band might be a proper choice for 3,4 content, along with the 910-cm^{-1} band for 1,2 content. Thus 1,2 content and 3,4 content could be determined from the total vinyl content. It is necessary to have well-characterized samples to calibrate this method before any quantitative measurements of configurational structure content can be made.

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(10) R. S. Sterns and L. E. Forman, *J. Polym. Sci.*, **26**, 381 (1959).