

Vibrational Spectra and Assignments of cis- and Trans-1,4-Polybutadiene*

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Received 06.10.2000

The Raman spectra of cis- and trans-1,4- polybutadiene were recorded in the region 100-4000 cm^{-1} and its infrared spectra were also measured in the wave number range 200–4000 cm^{-1} . The spectra were completely analysed. Probable assignments to observed bands were made with the help of intensities and normal co-ordinate analysis. The calculated normal frequencies were in good agreement with the experimental ones.

Key Words: Polymers, Infrared and laser raman spectra, Vibrational analysis.

Introduction

Polymer spectroscopists have studied widely the infrared spectra of the various crystalline diene polymers. But very little work has been done towards the analysis of the fundamental vibrations of diene polymers and copolymers. The title compound has been considered an important polymer because it has been widely used in industry as a synthetic rubber. In the present investigation, attempts were made to study the vibrational spectra of one such polymer, viz., 1,4-polybutadiene.

Cis-trans isomerism is a direct consequence of the high energy barrier to rotation at the double bond and is frequently encountered in unsaturated compounds. Groups around a C=C can be arranged spatially to give two types of isomers called the cis (Latin-on the same side) and trans (Latin-cross). The two forms have the same molecular formula but differ in configuration. The cis and trans isomers have different melting points and boiling points. The cis isomers have higher solubilities and greater dipole moments.

The infrared spectrum of syndiotactic 1,2-polybutadiene was analysed previously by Zerbi et al.¹. The IR and laser Raman spectra of syndiotactic-1,2-polybutadiene were analysed by Mohan et al.² and they made the vibrational assignments to various modes with the aid of normal co-ordinate analysis. Morero et al.³ have proposed a set of fundamental vibrations for cis- and trans-1,4-polybutadiene based on the study of its IR spectra. A vibrational analysis of crystalline trans-1,4-polybutadiene was carried out by Hsu et

*This paper has been presented at MBCAC III (3rd Mediterranean Basin Conference on Analytical Chemistry) 4-9 June, 2000 Antalya-Turkey

al.⁴ by analysing its IR and Raman spectra but they could not observe all the fundamental vibrations. Thus, a complete vibrational analysis of cis- and trans-1,4-polybutadiene is not available, to the best of our knowledge, in the literature. Hence, the present investigation was undertaken with the hope of providing more information on the fundamental vibrations as well as to assign all of them using the normal co-ordinate analysis through FT-Infrared and FT- Laser Raman spectroscopy.

Experimental

Spectroscopically pure chemicals were obtained from Aldrich Chemicals U.S.A. and used as such for recording spectra. The FT Raman spectra of cis- and trans-1,4-polybutadiene were recorded from solid phase samples on a Bruker IFS 66V with FRA 106 Raman module spectrophotometer using 1064nm output of a cw diode pumped Nd: YAG laser as a source of excitation in the region 100-4000 cm^{-1} operating at 200 mW power at the samples with a spectral resolution of 2 cm^{-1} . The infrared spectra were also recorded on Shimadzu-800, FTIR spectrometer series of Japan in the region 200-4000 cm^{-1} . The frequencies for all sharp bands are accurate to $\pm 1 \text{ cm}^{-1}$. The observed spectra are shown in Figures 1-4.

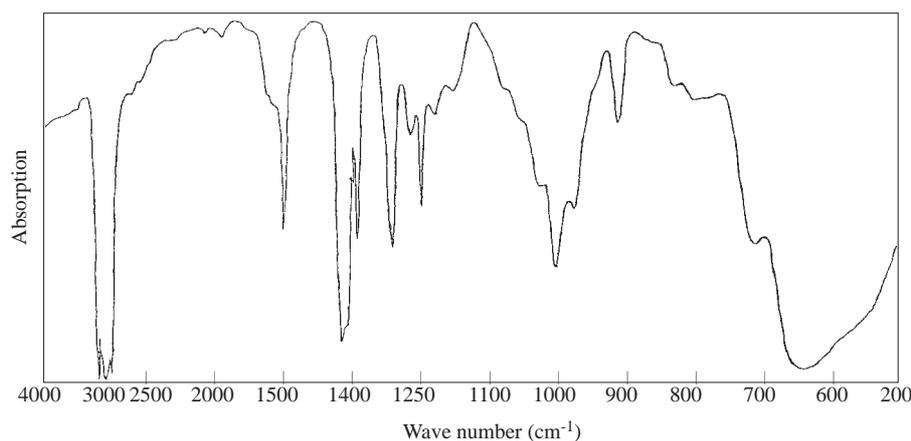


Figure 1. FT-Infrared Spectrum of Cis-1,4-polybutadiene.

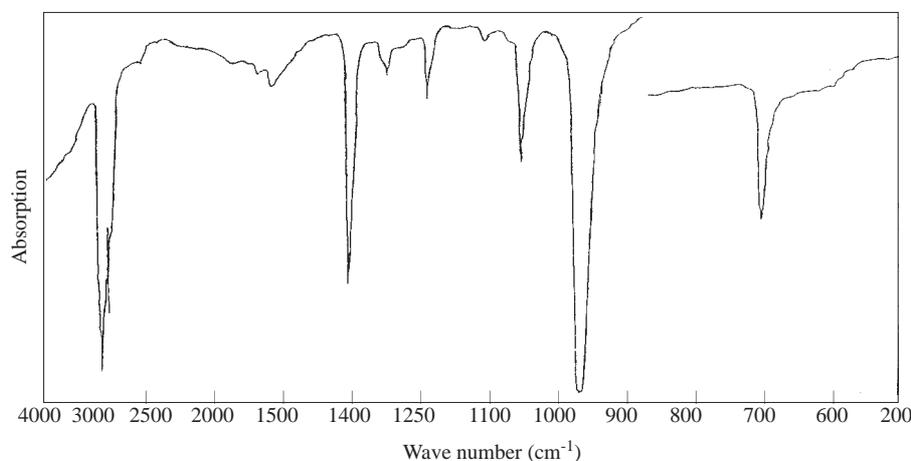


Figure 2. FT-Infrared Spectrum of Trans-1,4-polybutadiene.

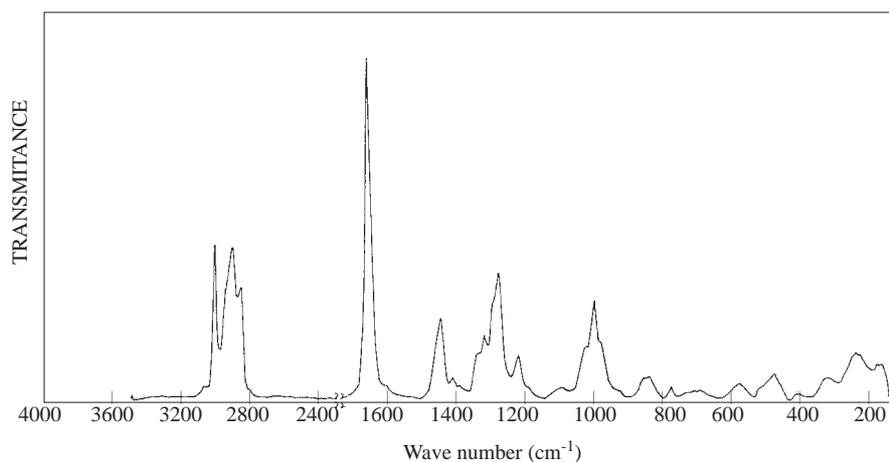


Figure 3. FT-Laser Raman of Cis-1,4-polybutadiene.

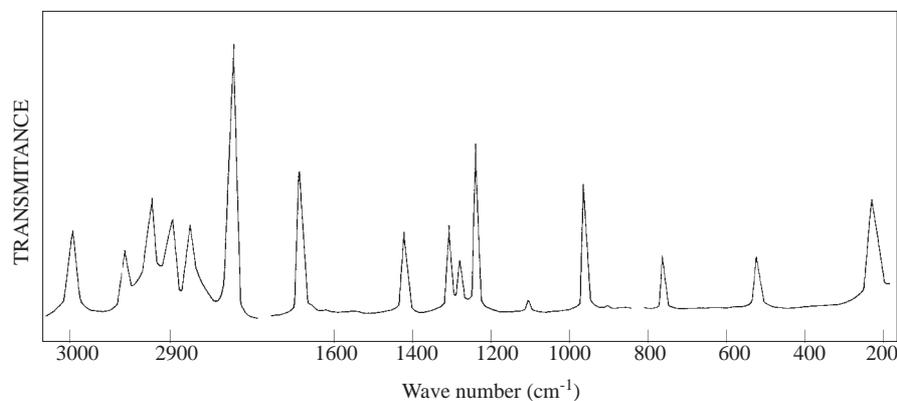


Figure 4. FT-Laser Raman of Trans-1,4-polybutadiene.

The values of bond-length and bond-angles were taken from Sutton's table⁵. Internal co-ordinates for the out-of-plane torsional vibrations are defined as recommended by IUPAC. The general quadratic valence force field was adopted for both in-plane and out-of-plane vibrations. The normal co-ordinate calculations were performed using the program given by Schachtschneider⁶. The initial sets of force constants were taken from the derivatives of allied molecules⁷. The calculated frequencies agree favourably with the observed frequencies, giving further support for the present assignment.

Results and Discussion

The observed frequencies along with their relative intensities of cis- and trans-1,4-polybutadiene and probable assignments are presented in Tables 1 and 2 respectively. The observed spectra are explained on the basis of C_{2v} point group symmetry for cis-1,4-polybutadiene and C_{2h} point group for trans-1,4-polybutadiene. The 56 optically active fundamental vibrations belonging to C_{2v} point group are

$$\Gamma_{vib} = 17 A_1 + 11 A_2 + 11 B_1 + 17 B_2$$

The 60 active vibrations of C_{2h} point group are distributed as

Table 1. Observed and calculated frequencies (cm^{-1}) and potential energy distribution of cis-1,4-polybutadiene.

Species	Observed frequency (cm^{-1}) and intensity		Calculated frequency (cm^{-1})	Assignment	(PED%)	
	Laser Raman	Infrared				
(1)	(2)	(3)	(4)	(5)	(6)	
A ₁		3070 VS	3064	=C-H stretching	90 ν_{CH}	
		3050 S	3048	=C-H stretching	92 ν_{CH}	
			2954	CH ₂ asymmetric stretching	84 ν_{CH_2}	
		2917 S	2908 VS	2912	CH ₂ asymmetric stretching	85 ν_{CH_2}
		2849 M	2845 VW	2853	CH ₂ symmetric stretching	71 $\nu_{CH_2} + 15\beta_{CH_2}$
		1650 VS	1659 S	1655	C=C stretching	78 $\nu_{CC} + 11\nu_{CC}$
		1440 M	1454 VS	1451	CH ₂ in-plane deformation	60 $\delta_{CH_2} + 21\nu_{CH}$
		1400 VW	1403 S	1408	CH ₂ in-plane deformation	46 $\delta_{CH_2} + 11\delta_{CH_2}$
		1340 W		1341	CH ₂ in-plane deformation	51 $\delta_{CH_2} + 19\delta_{CH_2}$
		1270 S	1227 VW	1284	CH ₂ in-plane deformation	60 $\delta_{CH_2} + 19\delta_{CH}$
		1210 W	1239 M	1242	CH ₂ rocking	36. $\rho_{CH_2} + 18.\delta_{CH_2} + 10.\nu_{CH}$
			1020 S	1026	C-C stretching	81 ν_{CC}
			1049 VW	1054	=C-H in-plane deformation	44 β_{CH}
		840 W	801 VW	844	CH ₂ rocking	28 ρ_{CH_2}
	A ₂			487	C=C-C deformation	32 δ_{CC}
			316	CH ₂ rocking	31 ρ_{CH_2}	
			180	C-C torsion	44 τ_{CC}	
			2841	CH ₂ stretching	69 ν_{CH_2}	
			1439	CH ₂ in-plane deformation	34 $\delta_{CH_2} + 31\delta_{CH_2}$	
			1424 W	1420	CH ₂ twisting	36 $\tau_{CH_2} + 26\omega_{CH_2}$
			1120 W	1104	CH ₂ twisting	41 $\tau_{CH_2} + 19\omega_{CH_2}$
			997 S	984	C-C stretching	71 ν_{CC}
			980 VW	971	CH ₂ wagging	31 $\omega_{CH_2} + 24\tau_{CH_2}$
			901 W	910	CH ₂ twisting	40 $\tau_{CH_2} + 22\omega_{CH_2}$
			678 VW	671	=CH out of plane deformation	36 $\eta_{CH_2} + 21\tau_{CH_2}$
			519 VW	511	C-C-C deformation	54 $\delta_{CCC} + 26\delta_{CCC}$
			321 W	316	C-C-C deformation	55 $\delta_{CCC} + 16\delta_{CH_2}$
			192 VW	198	C-C torsion	59 $\tau_{CC} + 14\delta_{CCC}$
B ₁				2909	CH ₂ stretching	76 $\nu_{CH_2} + 12\beta_{CH_2}$
			1318	CH ₂ wagging	51 $\omega_{CH_2} + 20\tau_{CH_2}$	
			1261	CH ₂ wagging	64 $\omega_{CH_2} + 18\tau_{CH_2}$	
			1120 VW	1111	CH ₂ twisting	44 $\tau_{CH_2} + 11\omega_{CH_2}$
			1065 VW	1061	CH ₂ wagging	51 $\omega_{CH_2} + 18\eta_{CH_2}$
				964	CH ₂ wagging	56 $\omega_{CH_2} + 21\eta_{CH_2}$
				804	CH ₂ rocking	55 $\rho_{CH_2} + 19\beta_{CH_2}$
			738 VW	731	=CH out of plane deformation	61 $\eta_{CH} + 24\eta_{CH_2}$
				579	C-C-C deformation	68 δ_{CCC}
				405	C-C-C deformation	74 δ_{CCC}
				190	C-C torsion	70 τ_{CC}
	B ₂			3065	=C-H stretching	81 ν_{CH}
				3054	=C-H stretching	71 ν_{CH}
				2991	CH ₂ stretching	78 ν_{CH_2}
				2910	CH ₂ stretching	81 ν_{CH_2}
			2832	CH ₂ stretching	75 ν_{CH_2}	
			1641	C=C stretching	86 ν_{CC}	
			1435	CH ₂ deformation	41 $\delta_{CH_2} + 21\omega_{CH_2}$	
			1332	CH in-plane deformation	48 $\beta_{CH_2} + 28\omega_{CH_2}$	
			1301	CH ₂ wagging	61 $\omega_{CH_2} + 14\delta_{CH}$	
			1191	C-C stretching	78 ν_{CC}	
			1112	CH ₂ wagging	49 $\omega_{CH_2} + 21\delta_{CH}$	
			1081	C-C stretching	71 $\nu_{CC} + 11\beta_{CCC}$	
			1009	C-C stretching	74 $\nu_{CC} + 14\beta_{CCC}$	
			772	C-C stretching	80 $\nu_{CC} + 11\beta_{CCC}$	
			574	C-C-C deformation	61 $\delta_{CCC} + 12\delta_{CC}$	
		352	C-C-C deformation	55 $\delta_{CCC} + 16\nu_{CC}$		
		279	C-C-C deformation	64 $\delta_{CCC} + 19\nu_{CC}$		

ν - Stretching β - In plane bending η - Out of plane bending
 ω - Wagging τ - Twisting/Torsion ρ - Rocking
 δ - Deformation

VS - Very Strong S - Strong M - Medium
 W - Weak VW - Very Weak

Table 2. Observed and calculated frequencies (cm^{-1}) and potential energy distribution of trans-1,4-polybutadiene

Species	Observed frequency (cm^{-1}) and intensity		Calculated frequency (cm^{-1})	Assignment	(PED%)
	Laser Raman	Infrared			
(1)	(2)	(3)	(4)	(5)	(6)
A_g	2998 M		3010	=CH stretching	$94\nu_{CH}$
	2920 M		2910	CH_2 asymmetric stretching	$80\nu_{CH_2}$
	2880 M		2906	CH_2 asymmetric stretching	$78\nu_{CH_2}+10\beta_{CH_2}$
	2840 VS		2842	CH_2 symmetric stretching	$71\nu_{CH_2}$
	1665 S		1668	C=C stretching	$74\nu_{CC}$
	1436 M		1446	CH_2 bending	$41\delta_{CH_2}+21\beta_{CH}$
	1427 VW		1434	CH_2 bending	$44\delta_{CH_2}+24\beta_{CH}$
	1330 M		1336	CH_2 wagging	$46\omega_{CH_2}+26\omega_{CH_2}+14\eta_{CH}$
	1310 M		1318	CH_2 twisting	$38\tau_{CH_2}+31\tau_{CH_2}+10\eta_{CH}$
	1269 S		1266	CH_2 wagging	$31\omega_{CH_2}+24\eta_{CH}+21\tau_{CH_2}$
	1153 W		1148	C-C stretching	$72\nu_{CC}$
	1016 S		1027	C-C stretching	$78\nu_{CC}$
	968 VW		964	CH_2 rocking	$58\rho_{CH_2}+21\beta_{CH_2}$
	540 M		552	C-C-C deformation	$39\delta_{CCC}+28\beta_{CCC}$
236 S		239	C-C torsion	$41\tau_{CC}+18\beta_{CC}$	
B_g	2998 M		3010	CH stretching	$86\nu_{CH}$
	2950 M		2961	CH stretching	$74\nu_{CH}$
	2920 S		2926	CH_2 asymmetric stretching	$71\nu_{CH_2}+20\beta_{CH_2}$
	2904 M		2917	CH_2 asymmetric stretching	$68\nu_{CH_2}+24\beta_{CH_2}$
	2849 VW		2851	CH_2 symmetric stretching	$75\nu_{CH_2}$
	1665 S		1668	C=C stretching	$86\nu_{CC}$
	1450 M		1446	CH_2 bending	$44\delta_{CH_2}+21\beta_{CH_2}$
	1429 M		1434	CH_2 bending	$51\delta_{CH_2}+14\beta_{CH_2}$
	1325 VW		1334	CH_2 bending	$50\delta_{CH_2}+12\beta_{CH_2}$
	1150 W		1143	C-C stretching	$84\nu_{CC}$
	1059 VW		1068	CH in-plane bending	$51\beta_{CH}+24\beta_{CH}$
	1020 S		1034	C-C stretching	$80\nu_{CC}$
	764 M		758	CH out-of-plane bending	$38\eta_{CH}+20\omega_{CH_2}+18\tau_{CH_2}$
	535 M		548	C-C-C deformation	$39\delta_{CCC}+24\beta_{CCC}$
240 S		243	C-C torsion	$42\tau_{CC}+18\beta_{CC}$	
A_u		2980 S	3002	=C-H stretching	$78\nu_{CH}$
		2945 M	2935	CH_2 asymmetric stretching	$81\nu_{CH_2}$
		2914 M	2916	CH_2 asymmetric stretching	$88\nu_{CH_2}$
		2895 VS	2890	CH_2 symmetric stretching	$91\nu_{CH_2}$
		2840 S	2844	CH_2 symmetric stretching	$89\nu_{CH_2}$
		1663 VW	1665	C-C stretching	$92\nu_{CC}$
		1550 W	1448	CH_2 bending	$57\delta_{CH_2}+22\beta_{CH}$
		1442 VS	1433	CH_2 bending	$55\delta_{CH_2}+18\beta_{CH}$
		1335 V	1328	CH_2 wagging	$55\omega_{CH_2}+22\tau_{CH_2}$
		1262 VW	1259	CH in-plane bending	$60\beta_{CH}+21\beta_{CH_2}$
		1130 VW	1141	C-C stretching	$84\nu_{CC}$
		1074 VW	1069	CH_2 twisting	$39\tau_{CH_2}+22\omega_{CH_2}$
		978 VS	979	C-C torsion	$48\tau_{CC}+21\beta_{CC}$
		963 VW	964	=C-H in-plane deformation	$54\beta_{CH}+24\beta_{CH_2}$
	774 M	781	CH_2 rocking	$56\rho_{CH_2}+20\beta_{CH}$	
B_u		2980 S	2990	=C-H stretching	$74\nu_{CH}$
		2915 M	2916	CH_2 asymmetric stretching	$68\nu_{CH_2}$
		2890 VW	2880	CH_2 symmetric stretching	$78\nu_{CH_2}+12\beta_{CH}$
		2841 VW	2844	CH_2 symmetric stretching	$81\nu_{CH_2}$
		1650 VW	1661	C-C stretching	$71\nu_{CC}$
		1446 VW	1440	CH_2 bending	$61\delta_{CH_2}+20\beta_{CH}$
		1312 W	1321	=C-H in-plane bending	$55\beta_{CH}+18\beta_{CH}$
		1237 W	1242	CH_2 wagging	$41\omega_{CH_2}$
		1123 VW	1128	C-C stretching	$71\nu_{CC}+11\beta_{CC}$
		1050 M	1064	C-C stretching	$74\nu_{CC}+14\beta_{CC}$
		1028 VW	1035	C-C stretching	$76\nu_{CC}$
		993 VW	985	C-C stretching	$84\nu_{CC}$
		776 VW	785	CH_2 rocking	$41\rho_{CH_2}+30\beta_{CH_2}+10\beta_{CH}$
		554 VW	551	C-C-C deformation	$28\delta_{CCC}+26\nu_{CC}+11\beta_{CC}$
	439 VW	427	C-C-C deformation	$34\delta_{CCC}+21\nu_{CC}+14\beta_{CC}$	

$$\Gamma_{vib} = 15 A_g + 15 B_g + 15 A_u + 15 B_u$$

All the modes are active in both Raman and infrared except A_2 mode which is infrared inactive for C_{2v} group while A_g , B_g , are inactive in IR and A_u , B_u are inactive in Raman for C_{2h} group. Assignments were made on the basis of relative intensities, magnitudes of the frequencies and polarization of the Raman lines.

Cis-1,4-Polybutadiene

Usually the band around 3000 cm^{-1} is assigned to CH stretching vibrations. In line with the above conclusion, the bands at 3070 and 3050 cm^{-1} are assigned to CH stretching vibrations. The medium bands at 1424 , 1120 and 901 cm^{-1} are assigned to CH_2 twisting modes. The CH_2 wagging vibrations are assigned to the bands at 1320 , 1262 , 1119 and 1065 cm^{-1} . The bands at 1210 and 809 cm^{-1} are assigned to CH_2 rocking vibrations. The above conclusions agree well with those of Srivastava *et al.*⁸.

The bands at 2994 , 2950 , 2908 and 2845 cm^{-1} are assigned to CH_2 stretching vibrations. The band at 1049 cm^{-1} is assigned to CH in-plane deformation. The band at 1340 cm^{-1} is assigned to CH_2 deformation. The above assignments are in good agreement with the literature values^[9,10].

The strong bands at 1659 and 1650 cm^{-1} are assigned to C=C stretching vibrations. The C-C stretching vibrations are assigned to the bands at 1196 and 1020 cm^{-1} . They agree favourably with those of Zwarich *et al.*⁹ and Green *et al.*¹⁰. The bands at 580 , 519 , 360 , 321 and 290 cm^{-1} are assigned to C-C-C deformation vibrations. The band at 486 cm^{-1} is assigned to C=C-C deformation vibration. The torsion vibrations usually occur below 200 cm^{-1} . In line with the above conclusion, the bands at 192 , 190 and 180 cm^{-1} are assigned to C-C torsion vibrations. They agree well with the literature values^[11,12].

Trans-1,4-Polybutadiene

The bands at 2998 , 2980 and 2950 cm^{-1} are assigned to CH stretching vibrations. The bands at 2914 , 2904 , 2895 and 2840 cm^{-1} are assigned to CH_2 stretching vibrations. These assignments are in good agreement with Srivastava *et al.*⁸. The strong Raman band at 1665 is assigned to C=C stretching while the bands at 1153 , 1054 and 1016 cm^{-1} are assigned to C-C stretching vibrations. The above conclusion agree favourably with those of Zwarich *et al.*⁹ and Green *et al.*¹⁰.

The normal co-ordinate analysis helps us to assign the medium bands at 1310 and 1074 cm^{-1} to CH_2 twisting modes. The bands at 1330 and 1237 cm^{-1} are assigned to CH_2 wagging modes. These assignments agree favourably with those of Tadokoro *et al.*¹¹ and Zerbi *et al.*¹². The remaining bands are assigned to C-C-C deformation, C-C torsion, CH in-plane deformation and CH_2 rocking.

Cis- and Trans-1,4-Polybutadiene

The trans-1,4-polybutadiene which possesses a dipole moment equal to zero does not show stretching of the double bond and hence the band corresponding to C=C stretching is not found in its IR spectra. On the other hand, cis shows a strong C=C absorption around 1659 cm^{-1} . The maximum frequency (ν_{max}) corresponding to =C-H bending¹³ is observed at 1049 cm^{-1} for cis and it is observed at 1312 cm^{-1} in its IR spectra of trans-1,4-polybutadiene. The characteristic band appears at 963 cm^{-1} in the IR spectra of

trans configuration, whereas no such band is observed in the range of 960–970 cm^{-1} of the IR spectra of cis configuration.

Potential Energy Distribution

To check whether the chosen set of assignments contributes the maximum to the potential energy associated with normal co-ordinates of the molecules, the potential energy distribution (PED) was calculated using the relation

$$\text{PED} = F_{ii} L_{ik}^2 / \lambda_k$$

where F_{ii} are the force constants defined by the damped least square technique, L_{ik} the normalised amplitude of the associated element (i,k) and λ_k the eigen value corresponding to the vibrational frequency of the element k. The PED contributions corresponding to each of the observed frequencies over 10% are only listed in the present work.

Conclusion

A complete vibrational spectra and analysis are available in the present work for cis- and trans-1,4-polybutadiene. The close agreements between the observed and calculated frequencies confirm the validity of the present assignment.

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