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Vibrational Spectroscopic Studies On Cis-1,4-Polychloroprene

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Abstract: Fourier transform infrared spectra of cis -1,4-polychloroprene was recorded in the region of 400-4000cm^{-1} and its Raman spectra was also recorded in the wave number range of 100-4000cm^{-1}. The spectra were completely analyzed. Probable assignments to observe bands were made with the aid of intensities and normal coordinate analysis by assuming C_s symmetry. The simple general valance force field (SGVFF) was employed in normal coordinate analysis to calculate the potential energy distribution (PED) for each fundamental vibration. The PED contributions corresponding to each of the observed frequencies give the purity of the modes in spectral analysis.

Keywords: FTIR, FT Raman, cis-1,4-polychloroprene, PED, vibrations..
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Introduction and Experimental

Polychloroprene (PCP) or neoprene, was discovered 65 years ago and has been used as a base polymer for contact adhesives for at least 60 years[1]. PCP is available either as a dry polymer or as latex[2]. PCP happens to be the first synthetic elastomer to be successfully commercialized as an oil-resistant substitute for natural rubber. Polychloroprene is also noted for its high durability under harsh conditions making it a much needed materials[3]. To date, reports indicate that PCP adhesives have many advantages compared to other alternative adhesives[4]. For ecological and work place hygiene reasons, solvent-free adhesives based on water-borne polychloroprene dispersions are increasingly being developed. Water based PCP adhesives offer an unsurpassed combination of advantages for the adhesive formulator[1].The vibrational spectra of poly chloroprene in the gaseous, liquid, solid, solution and argon matrix phase was analyzed by Compton *et al.*[5] Investigation by Yunshu *et al.*[6] established the tensile strength of cross linked poly chloroprene by radiation induced cross linking of polychloroprene.

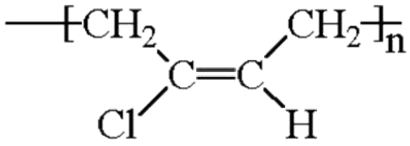

Figure 1 Structure of cis-1-4 polychloroprene.

A vibrational analysis of semi crystalline and amorphous trans polychloroprene was carried by Wallen[7] using Raman spectra and related it with the molecular model for the structure of the crystalline trans-1, 4-polychloroprene unit. Analysis of infrared spectra of polychloroprene polymerized at different temperature was carried out by Tabb *et al.*[8] It was found that there were significant structural irregularities as the polymerization temperature is raised. Studies using Nuclear Magnetic Resonance (NMR) spectra of poly chloroprene were conducted. NMR analysis of the microstructure of poly (chloroprene sulfone) and study of sequence distribution of chloroprene and methyl methacrylate copolymers were conducted by Okada & Otsuru.[9] To date, a complete vibrational analysis of cis-1,4-polychloroprene is not available in the literature to our knowledge. Our work represents the first complete experimental and theoretical investigation of cis-1, 4-polychloroprene. The spectra have been qualitatively analyzed in terms of peak position and intensities. Thus, this investigation was conducted with the hope of providing complete information on the fundamental vibrations as well as to assign all of them using the normal co-ordinate analysis and FT-Infrared and FT-Raman spectroscopy. Cis-1, 4-polychloroprene.was obtained from MS Aldrich with high purity and used as such without further purification to record the spectra. The FTIR spectrum of this compound has been recorded in the region 400-4000 cm^{-1} by a Brukker IFS 66V spectrometer with a scanning speed of $30cm^{-1}$ min^{-1} with a spectral width of $2.0cm^{-1}$. The FT Raman spectrum of poly chloroprene was also recorded in the same instrument with a FRA 106 Raman module equipped with Nd:YAG laser source operating at 1.064μm line with 200 mW power in the wave number range 4000 – 100 cm^{-1}. The frequencies of all sharp bands were accurate to ± 1 cm^{-1}.

Normal Coordinate Analysis

The structure of cis-1,4-polychloroprene is show in Figure 1. The maximum number of potentially active observable fundamentals of a polymer in which the chemically repeating unit of a polymer chain contains N atoms is equal to (3N-4), ignoring three translational degrees of freedom and rotation of the polymer molecule about its own axis. The normal co-ordinate analysis of Fuhrer et al,[10] was used after a suitable modification to calculate vibrational frequencies and potential energy distributions (PED). This program follows the Wilson F-G matrix method[11-13] of vibrational analysis in which the normal coordinates are defined with respect to a set of molecular internal coordinates. The theoretical calculations on the vibrational modes are made by an appropriate model of the conformation of the polymer chain. The molecule under investigation, poly chloroprene possesses a C_s symmetry. The structural parameters necessary for this compound is taken from the Sutton table[14]. The observed spectrum is explained on the basis of C_s point group symmetry. The 26 fundamental vibrations are distributed as $\Gamma_{vib} = 18a' + 8a''$.All vibrations are both infrared and Raman active. The observed frequencies have been assigned to various modes of vibration on the basis of intensity, frequency and normal coordinate analysis. To obtain a fair agreement between observed and theoretical frequencies, the simple general valance force field (SGVFF) method was adopted for both in plane and out of plane vibrational modes. In SGVFF force field, the valance force constants can also be transferred between the structurally related molecules, which are found to be useful in the normal coordinate analysis. The PED calculated using the final set of force constants are presented in Table 1.

Results and Discussion

Stretching Vibrations

Based on the knowledge of the vibrations of hydrocarbon, carbon-hydrogen stretching vibrations of an unsaturated group such as an alkenic moiety (=C-H) or an aromatic hydrocarbon is expected to appear around 3050 cm^{-1}. In line with this notion, the band at 3020 cm^{-1} in the infrared spectra and 3013 cm^{-1} in the Raman spectra is assigned to =C-H stretching vibration. As expected these modes are pure stretching modes. Symmetrical bonds such as C=C and C-C manifest themselves by giving the most intense bands in Raman spectra[15]. The C=C stretch can readily be assigned to the very strong band in the Raman spectra at $1660cm^{-1}$. The infrared counter part for this mode has also been identified at $1660cm^{-1}$ [16]. The medium strong Raman band and IR band at $1000cm^{-1}$ is assigned to C-C stretching. Another skeletal mode containing significant contributions of C-C is assigned to the bands at $1107cm^{-1}$ in the IR spectra. The above conclusions agree favorably with those of Mas Rosemal et al.[17] and Green & Harrison [18].

Methylene Modes

The Raman bands at 2906 and $2846cm^{-1}$ and IR bands at 2920 and $2840cm^{-1}$ are assigned to CH_2 asymmetric stretching vibrations. The IR bands at 2660 and $2527cm^{-1}$ are assigned to CH_2 symmetric stretching vibrations. The methylene bending mode is commonly ascribed to a strong infrared band near $1475cm^{-1}$ [19]. The very strong IR band at $1433cm^{-1}$ is assigned to CH_2 deformation. The medium strong Raman band at $1447cm^{-1}$ is also assigned to CH_2 deformation mode in line with Nielson and Woollett [20]. The bands at 820 and $773cm^{-1}$ in the IR and 820 and $770cm^{-1}$ in the Raman spectra were assigned to CH_2 rocking. This is in agreement with Edwards [21].The twisting and wagging CH_2 normal modes occurs between 1151cm^{-1} and 1350cm^{-1}. The CH_2 wagging modes are identified at medium IR band at 1300cm^{-1} and at medium Raman band at 1280cm^{-1}. CH_2 twisting mode is assigned to 1220cm^{-1}, 1213cm^{-1} and 1200cm^{-1}. The above conclusions agree well with those of Mas Rosemal and Kathiresan [22].

Table 1 Observed and theoretical wave numbers (cm^{-1}) and potential energy distribution (PED) for 1,4 cis poly chloroprene

Species	Observed frequency		Calculated wave number	Assignment	% PED
	FTIR	FTR			
	3300 w			2527 + 773	-
a’	3013 ms	3020 m	3015	=C-H stretching	96ν CH
a’	2920 vs	2906 s	2914	C-H asym stretching in CH_2	91νas CH
a’	2840 s	2846 m	2841	C-H asym stretching in CH_2	89νas CH
a’	2660 vw		2654	C-H sym stretching in CH_2	87νsym CH
a’	2527 vw		2520	C-H sym stretching in CH_2	94νsym CH
	1693 ms			1346 x 2 - 1000	-
a’	1660 vs	1660 vs	1658	C=C stretching	84γCC + 10γCH
	1483 w			822 + 655	
a’		1447 m	1440	CH_2 deformation	74δCH_2 + 16ρCH_2
a’	1433 vs	1430 ms	1428	CH_2 deformation	80δCH_2 + 12ρCH_2
a’	1346 m	1337 m	1341	=C-H in plane bending	81βCH + 10βCC
a”	1300 m		1292	CH_2 wagging	66ωCH_2 + 20τCH_2
a”		1280 m	1270	CH_2 wagging	71ωCH_2 + 18τCH_2
a”	1220 w	1213 w	1215	CH_2 twisting	68τ CH_2 + 28ωCH_2
a”	1200 vw		1189	CH_2 twisting	64τ CH_2 + 20ωCH_2
a’	1107 ms		1101	C-C stretching	74ν CC + 14ν CC
a’	1000 m	1000 ms	992	C-C stretching	78ν CC + 10ν CC
a”	880 w		882	=C-H out of plane bending	66η CH + 21ν CC
a’	822 s	820 w	817	CH_2 rocking	60ρ CH_2 + 28δ CH_2
a’	773 m	770 w	772	CH_2 rocking	68ρ CH_2 + 20δ CH_2
		660 w		1660 - 1000	-
a’	653m		648	C-Cl stretching	82ν CCl + 14ν CC
a’		600 w	582	C-CH_2 in plane bending	79β CCH_2 + 20β CC
a’		567 w	556	C-CH_2 in plane bending	71β CCH_2 + 18β CC
a’		480 m	472	C=C-C deformation	51δ C=C-C + 20β C-Cl + 10β CH
a’		367 w	361	C-Cl in plane bending	60β C-Cl + 21β CC
a”		340 w	333	C-CH_2 out of plane bending	50η CCH_2 + 18η CCC
a”		213 w	209	C-CH_2 out of plane bending	52η CCH_2 + 17η CCC
a”		147 w	141	C-Cl out of plane bending	48η C-Cl + 19η CCC

vs, very strong; s, strong; ms, medium strong; m, medium; w, weak; vw, very weak; ν, stretching; δ, deformation; β, in-plane bending; η, out-of-plane bending; ρ, rocking; ω, wagging; τ, twisting

In-Plane and Out-of-Plane-Bending

The C-H in-plane band is assigned to medium intensity, polarized line in the Raman spectrum at 1337cm^{-1}. The corresponding mode in the infrared spectrum appears as a medium band at 1346cm^{-1}. This vibration appears in the expected range and finds support from literature values [23]. The C-H out of plane bending is assigned to 880cm^{-1} in the IR spectra which agrees well with Samuel and Mohan [24].

In a halogen containing compounds, C-Cl stretching vibration is expected in the range of 800cm^{-1} to 600cm^{-1}. The medium intensity band at 655cm^{-1} in the IR spectra is identified as C-Cl stretching [25]. The in-plane and out-of-plane bending of C-Cl is assigned to 367 and 141cm^{-1} in the Raman spectra. Five fundamentals are calculated below 600cm^{-1} in the Raman spectra. The C=C-C deformation is assigned to a medium intensity band at 480cm^{-1} which agrees well with Nallasamy et al [26]. The C-CH$_2$ in- plane bending bands are assigned to weak bands at 600 and 567cm^{-1} and out-of-plane bending are assigned to 340 and 213cm^{-1} respectively.

Potential Energy Distributions

The potential energy distribution is expressed in terms of the percentage contribution of normal coordinates or symmetry coordinates to the potential energy of each normal mode. The potential energy distribution (PED) has been calculated using the relation

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

where F_{ii} are the final force constants, L_{ik} the transformation matrix of the associated element (i,k) and λ_k, the eigen value for the corresponding vibrational frequency of the element k. The potential energy distribution calculated confirms the validity of the assignments. In the normal coordinate analysis potential energy distribution plays an important role for the characterization of the relative contributions from each internal coordinate to the potential energy associated with a particular normal coordinate of the molecule. The contribution to the potential energy from the individual diagonal elements gives rise to a conceptual link between the empirical analysis of the vibrational spectra of complex molecules dealing with the characteristic group frequencies and the theoretical approach from the computational of the normal modes. The PED contributions corresponding to each of the observed frequencies are listed in Table 1

Conclusions

A complete vibrational spectra and analysis is available in the present work for 1, 4 cis poly chloroprene. The close agreement between the observed and calculated frequencies and PED calculations confirm the validity of the present work.

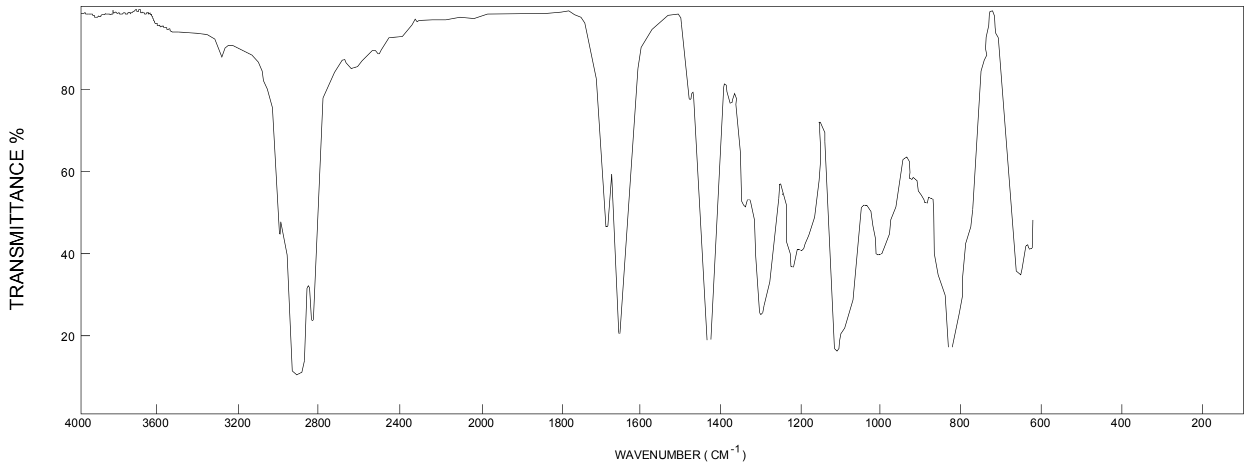

FIG 2 : FT - IR SPECTRUM OF CIS 1,4 - POLYCHLOROPRENE

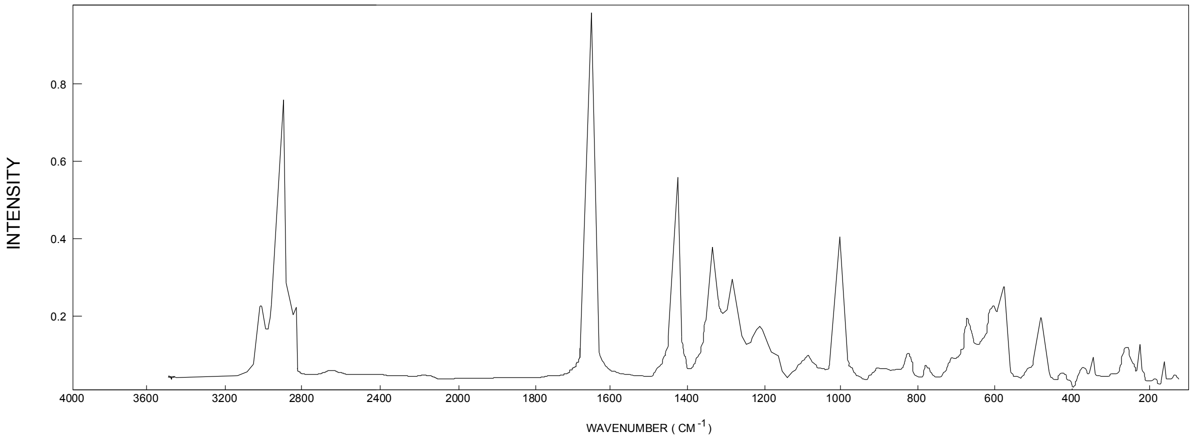

FIG 3 : FT - RAMAN SPECTRUM OF CIS 1,4 - POLYCHLOROPRENE

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