Vibrational Spectroscopic Studies on Trans-1,4-Polychloroprene

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Fourier transform infrared and Raman spectra of trans-1,4-polychloroprene have been recorded in the range of 4000-400 and 3500-100 cm^{-1}, respectively. In the present investigation, detailed assignments of the observed fundamental bands of trans-1,4-polychloroprene were analysed in terms of peak positions and relative intensities. In the hope of providing more effective information on the fundamental vibrations, a normal coordinate analysis was performed on trans-1,4-polychloroprene, by assuming C$_S$ symmetry. The simple general valance force field (SGVFF) was employed in normal coordinate analysis and to calculate the potential energy distribution (PED) for each fundamental vibration. The PED contribution corresponding to each of the observed frequencies shows the reliability and accuracy of the spectral analysis.

Key Words: FTIR, FT-Raman, spectra, trans-1,4-polychloroprene, PED, vibration.

Introduction

Vibrational spectroscopy plays a prominent role in the research and development of polymers. It provides useful information on their chemical, conformational, crystal and morphological structure. The study of elastomers by Raman spectroscopy has been desirable for a long time. It has allowed quantitative work on blends and isomeric elastomers and also the direct study of the rubber vulcanisation process. Problems associated with fluorescence, exaggerated by the presence of impurities in the elastomer and the addition of cross-linking materials and anti-detergents, have meant that the vibrational spectra of elastomers have been limited to IR spectroscopy. In conventional Raman spectroscopy, materials have been specially selected to be of low fluorescence and have undergone extensive preparation before examination[1]. This is particularly unfortunate as the technique, with its high sensitivity to the non-polar species (C=C and C−S) which

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make up polymer chains and the products of vulcanisation, has obvious potential advantages over the complementary technique of IR spectroscopy.

Raman spectroscopy with a laser source finds extensive application in analysing the vibrational spectra of polymers in conjuction with infrared spectroscopy. Vibrational modes important for configurational and conformational studies are often weak or inactive in the infrared, while these bands are strong in the Raman effect. For many polymers, bands inactive in the infrared are active in Raman, and vice versa. Improved polarisation devices and techniques have made orientation studies more meaningful. Absorption by polymers in the far infrared is due to the low frequency vibration of heavy atoms or groups and is weak in intensity.

Recent advances, which combined the use of a near infrared excitation source with Fourier transform collection techniques[2,3] to produce Raman spectra, have enabled these problems to be substantially reduced or to be overcome completely. This has triggered a re-evaluation of the role of Raman spectroscopy in the study of elastomers.

The combined use of IR and Raman spectroscopy extracts most of the obtainable information, and these are popular tools in the arsenal of the polymer scientists. Various crystalline polymers have been widely investigated by several spectroscopists. However, very little work has been done towards the analysis of the fundamental vibrations of the polymers. IR and Raman spectroscopic methods have contributed substantially to our understanding of the behaviour of polymers such as polyethylene[4], polypropylene[5], polyvinyl chloride[6,7] and polymerised 1,3-dienes[8−10].

The presence of conformational equilibrium for a compound normally results in measurable changes in the physical properties of that compound, such as the vibrational, electronic and rotational spectra and kinetic and thermodynamic properties. The mono-substituted 1,3-dienes such as isoprene and chloroprene are polymerised in different forms. Chloroprene, or 2-chloro-1,3-butadiene, is a volatile liquid monomer used extensively in the manufacture of polychloroprene (neoprene) elastomer. It is known that polychloroprene has a highly regular structure primarily made up of linear sequences of trans-2-chloro-2-butylene units, as shown in Figures 1(a) and 1(b), and represents the schematic model of repeat unit of trans-1,4-polychloroprene. However, other possible structural isomers can also be observed in polychloroprene.

Polychloroprene is the only widely used polymer in many industrial applications. In addition to butadiene and isoprene, chloroprene is an important monomer constituting many elastomeric materials. The uses of polychloroprene are numerous and widespread. Chloroprene rubber has excellent resistance to oil, chemicals and deterioration, in addition to having flame-retarding properties. It is widely used in automobile parts and in a variety of heavy-duty equipment. Despite its cost, its high durability under harsh conditions makes neoprene rubber a much-needed material. Neoprene rubber has excellent solvent resistance potential, i.e. the ability to withstand conditions imposed upon it without experiencing any substantial change in its properties over the period of exposure. It is therefore used in the chemical engineering industry for lining the insides of vessels/containers which may contain solvents/solutions/reagents. In brief, polychloroprene is used for making hoses, gaskets, tubing for carrying corrosive gases and oils, conveyer belts, linings for reaction vessels, adhesives, etc.
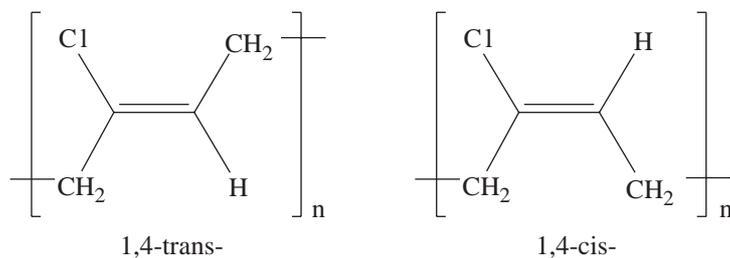
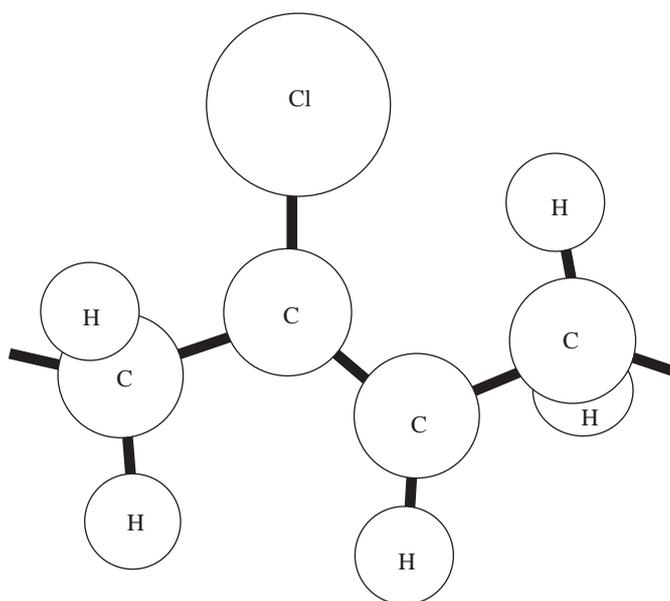**Figure 1a.** Structure of cis- and trans-1,4-polychloroprene.

Figure 1b. Model of repeating unit of trans-1,4-polychloroprene.

Baah and Baah[11] reported the results of chemical attacks by organic reagents on neoprene, nitrile and natural rubbers, and found that the mass of rubber specimens increased for the duration of the experiment with the exception of the neoprene rubbers. Compton et al.[12] analysed the vibrational spectra of 2-chlorobuta-1,3-diene in the gaseous, liquid, solid, solution and argon matrix phases. Radiation-induced cross-linking of polychloroprene containing nine different polyfunctional monomers has been investigated by Yunshu et al.[13], who established the tensile strength of cross-linked polychloroprene.

Tabb et al.[14] analysed the infrared spectra of polychloroprene polymerised at different temperatures and interpreted the spectral differences among the polychloroprenes in terms of the increase in structural irregularities that occur as the polymerisation temperature is raised. Wallan et al.[15] compared the spectral changes in both sets of Raman data for semi-crystalline and amorphous polychloroprene to the vibrations calculated for the crystalline trans-polychloroprene unit and then related these to the molecular model for the structure of the crystalline trans-1,4-polychloroprene unit.

Coleman et al.[16] obtained the vibrational spectrum of the crystalline regions of semi-crystalline polychloroprene by employing an absorption subtraction routine to remove the absorbance contribution of the amorphous regions of the polymer. Tabb and Koenig[17] reported the absorbance subtracted crystalline spectrum and carried out a normal coordinate analysis of polychloroprene and compared the calculated frequencies to the experimental values obtained.

Until now, complete vibrational spectroscopic studies of trans-1,4-polychloroprene had not received much attention from either the experimental or theoretical viewpoints. Our work represents the first complete experimental and theoretical investigation of trans-1,4-polychloroprene. The spectra have been qualitatively analysed in terms of peak positions and intensities. With the help of the added data and the utilisation of group theory and normal coordinate analysis, an attempt has been made to achieve a more satisfactory interpretation of the spectra of trans-1,4-polychloroprene.

Experimental

Solid trans-1,4-polychloroprene was obtained from M/S Aldrich Chemicals, USA, had a stated purity of 99% and was used as such without further purification to record the spectra. The FTIR and the FT-Raman spectra of trans-1,4-polychloroprene were recorded as films. These were prepared by dissolving the compound in CS_2, pouring it onto a glass plate and evaporating off the solvent. The films were finally dried in an oil vacuum at a slightly elevated temperature. The FTIR spectrum of this compound was recorded in the region of 4000–400 cm^{-1} by a Bruker IFS 66V spectrometer of spectral width 2.0 cm^{-1}. The FT-Raman spectrum was also recorded on the same instrument, with an FRA 106 Raman module equipped with an Nd:YAG laser source operating at a 1.064 μm line with 200 mW power in the wavenumber range 4000–100 cm^{-1}. The frequencies of all sharp bands were accurate to ± 1 cm^{-1}.

Normal Coordinate Analysis

In order to derive strict selection rules for the vibrational spectra of polymers, it is necessary to make two assumptions: (1) that the polymer molecules are infinitely long and (2) that these polymer molecules have a regular arrangement in a crystalline lattice. Consider a crystalline polymer in which the chemically repeating unit of a single polymer chain contains N atoms. The maximum number of potentially active observable fundamentals of the repeating unit is (3N–4), ignoring three translational degrees of freedom and the rotation of the polymer molecule about its own axis. The selection rule for this simplified model may be derived from an analysis of the factor group of the one-dimensional space group[18], and it is legitimate to start the correlation of theory and experiment at this point.

The normal coordinate analysis of polychloroprene is essential in order to elucidate the relationship between the molecular structure and vibrational spectra of the polymer. The earlier work on the interpretation of the vibrational spectra of polychloroprene[17] is not complete. With the aim of gaining more complete knowledge of the vibrational spectra of polychloroprene, a normal coordinate calculation is carried out using Wilson's FG matrix method[19−21] with the aid of the computer program developed by Fuhrer et al.[22], with suitable modification to calculate the vibrational frequencies and potential energy distribution (PED). For the normal coordinate analysis of polymers, force constants must be approximated from values obtained from the analysis of suitable model compounds[17]. The theoretical calculations of the vibrational modes can be made by an appropriate model of the conformation of the polymer chain. In such an approach it is imperative that a reliable force field be available so that the molecular motions can be accurately described. The validity of the force constants chosen can be evaluated by a comparision between the observed and calculated frequencies. Trans-1,4-polychloroprene possesses C_S point group symmetry by assuming CH_2 groups as point masses lying in the plane of the molecule. The distribution of the normal modes among the

irreducible representations for this C_S symmetry is given by $\Gamma_{vib} = 17a' + 9a''$. All vibrations are active in both IR and Raman. Most of the force field generally ignores the interaction between the neighbouring stretching vibrations and between bending vibrations. Therefore the average distortion between the calculated and the observed frequencies is usually large. To obtain a fair agreement between the theoretical and observed frequencies, the simple general valance force field (SGVFF) was adopted for both in-plane and out-of-plane vibrational modes, in which the valance force constants can also be transferred between structurally related molecules, which is very useful in normal coordinate analysis. The force constants were refined by the damped least-square technique[23] until a satisfying agreement was established between the theoretical and observed frequencies. The PEDs calculated using the final set of force constants are presented in the table.

Results and Discussion

The FTIR and FT-Raman spectra of trans-1,4-polychloroprene are shown in Figures 2 and 3. The observed spectra of the compound were analysed on the basis of C_S point group symmetry by assuming CH_2 groups as point masses. The observed and calculated frequencies of trans-1,4-polychloroprene in the infrared and Raman along with their relative intensities and proposed assignments are summarised in the table. Assignments have been made on the basis of relative intensities, magnitude of frequencies and mainly on the normal coordinate calculations as well as the literature data of polymers of similar structure. The purity of the normal modes is further confirmed by calculating the PED to each fundamental vibration.
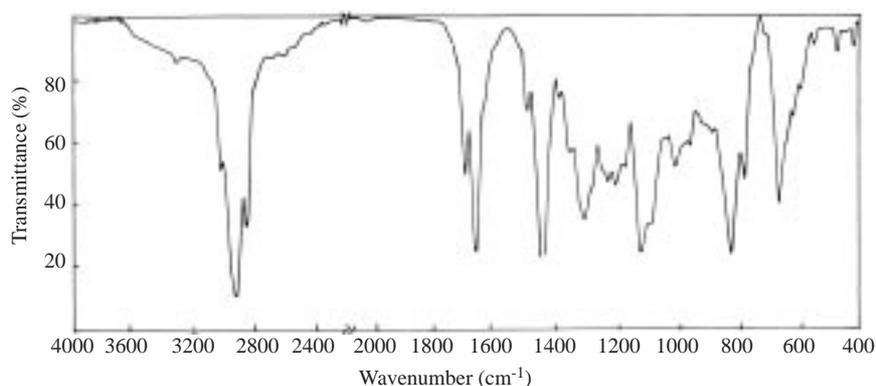

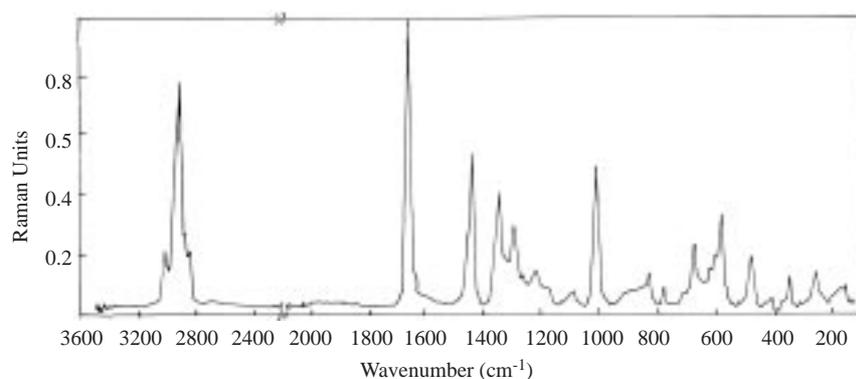**Figure 2.** FTIR spectrum of trans-1,4-polychloroprene.

Figure 3. FT-Raman spectrum of trans-1,4-polychloroprene.

The numerous C−H modes found in trans-1,4-polychloroprene arise from the presence of two proton types, methylene and methine. The C−H stretching frequency is normally placed between 3100 and 2800 cm^{-1}. The strong infrared and medium Raman bands which appear at 3022 and 3023 cm^{-1} respectively have been attributed to the =C−H stretching mode, as the corresponding force constant contributes almost 100% PED of this mode. The =C−H out-of-plane bending vibration occurs between 1000 and 800 cm^{-1}. The =C−H out-of-plane bending vibration is assigned to 887 cm^{-1} in the infrared. The normal coordinate analysis shows that this mode is highly mixed with the twisting and wagging out-of-plane bending vibrations of the methylene group. The in-plane bending vibration of the methine C−H is at 1210 cm^{-1} in the infrared and 1216 cm^{-1} in Raman. This vibration is also overlapped to some extent with the rocking and deformation vibrations of the methlene group. These assignments are in good agreement with the literature[9,24].

The methylene (CH$_2$) stretching typically appears in the region 3000-2800 cm^{-1}. A detailed investigation of the asymmetric stretching, ν_a(CH$_2$), and symmetric stretching, ν_s(CH$_2$), and the internal modes of the CH$_2$ groups has been carried out, and the assignments for these bands in the spectra have been satisfactorily made, by expecting asymmetric stretching to be much more intense than symmetric stretching. The frequencies seen at 2932 and 2916 cm^{-1} in the IR, and 2914 cm^{-1} in the Raman correspond to ν_a(CH$_2$). The frequencies observed at 2857 cm^{-1} in the IR and at 2860, and 2841 cm^{-1} in the Raman correspond to ν_s(CH$_2$). It is clear from the potential energy calculation that the frequencies above 1660 cm^{-1} are dominated by single vibrational modes, i.e., the contribution of potential energy arising from the remaining force constants to these normal modes is negligible.

The well established deformation vibrations, δ(CH$_2$), give rise to absorption in the region 1500−1400 cm^{-1}. The strong band at 1432 cm^{-1} in the Raman and the very strong and medium bands at 1488 and 1433 cm^{-1} in the IR are assigned to the deformation δ(CH$_2$) modes of methylene groups. From the potential energy distribution calculation, it is clear that the methylene rocking modes and the in-plane bending of the neighbouring bonds also contribute to the CH$_2$ deformational vibrations. The rocking vibrations of the CH$_2$ group are much more susceptible to the influence of neighbouring groups than the scissoring vibrations. It would be anticipated that methylene groups vicinal to polar groups in such structures as –O−CH$_2$−, −C=C−CH$_2$− and –CO−CH$_2$− would show characteristic rocking bands. This is moderately strong in the infrared and weak in the Raman. The rocking mode of the CH$_2$ group gives rise to the medium bands at 826 and 783 cm^{-1} in the Raman and strong bands at 826 and 780 cm^{-1} in IR spectra. This is moderately coupled with the deformational mode of the CH$_2$ group. The assignments of the remaining active fundamentals, the CH$_2$ wagging and twisting, occur over a frequency range centred about 1300 cm^{-1}. The medium and weak bands observed at 1285, 1250 and 1254 cm^{-1} are assigned to the methylene twisting modes. The twisting mode is highly coupled with the wagging mode of the CH$_2$ group. The peaks seen at 1345, 1337 and 1302 cm^{-1} in the IR and in the Raman are considered to be the CH$_2$ wagging modes. Similarly, the normal coordinate analysis data show that the wagging fundamental vibrations overlap moderately with the twisting vibration of the CH$_2$ group[25]. The C=C stretching frequency typically appears between 1680 and 1630 cm^{-1}. In the present spectra the very strong band observed at 1659 cm^{-1} in the IR and 1660 cm^{-1} in the Raman is assigned to the C=C stretching mode and is in good agreement with the literature[10,26].

The bands appearing in the region 1100–900 cm^{-1} are associated with C–C skeletal stretching modes. In the IR spectrum, the methylene vibrations are clearly the strongest, but the C−C modes dominate the Raman spectrum. In the present work, the strong and medium intensity infrared bands at 1100 and 1004

cm^{-1} and the bands found at 1084 and 1005 cm^{-1} in the Raman spectra are ascribed to C−C stretching vibrations. The C−Cl stretching region between 800 and 600 cm^{-1} is well known for its resonance specific to configurational/conformational structures of trans-1,4-polychloroprene. The strong band at 669 cm^{-1} in the infrared and the medium intensity band observed at 670 cm^{-1} in the Raman spectra are assigned to the C−Cl stretching mode. The in-plane and out-of-plane vibrations of C−Cl bond are given in the Table.

Table. Observed and calculated wavenumbers (cm^{-1}) and PED for trans-1,4-polychloroprene[a].

Species	Observed wavenumber/int		Calculated wavenumber	Assignment	% PED
	FTIR	FTR			
a′	3022 s	3023 m	3029	=C-H stretching	$91 \, \nu_{CH}$
a′	2932 vs	—	2921	CH_2 asymmetric stretching	$65\nu_{CH_2} + 21\nu_{CH}$
a′	2916 vs	2914 vs	2907	CH_2 asymmetric stretching	$76\nu_{CH_2} + 18\nu_{CC}$
a′	2857 s	2860 m	2850	CH_2 symmetric stretching	$71\nu_{CH_2} + 22\nu_{CH}$
a′	—	2841 w	2832	CH_2 symmetric stretching	$68\nu_{CH_2} + 19\nu_{CC} + 10\nu_{C-Cl}$
a′	1659 s	1660 vs	1656	C=C stretching	$87\nu_{CC} + 10\nu_{CH_2}$
a′	1488 m	—	1470	CH_2 deformation	$68\delta_{CH_2} + 14\rho_{CH_2} + 15\beta_{C-Cl}$
a′	1433 vs	1432 s	1425	CH_2 deformation	$58\delta_{CH_2} + 20\rho_{CH_2} + 11\beta_{CH}$
a″	1345 m	1337 m	1336	CH_2 wagging	$64\omega_{CH_2} + 17\tau_{CH2} + 10\gamma_{C-Cl}$
a″	1302 w	—	1286	CH_2 wagging	$56\omega_{CH_2} + 26\tau_{CH2} + 12\gamma_{CH}$
a″	1285 m	1285 m	1281	CH_2 twisting	$55\tau_{CH2} + 18\omega_{CH_2} + 21\gamma_{C-Cl}$
a″	1250 w	1254 w	1248	CH_2 twisting	$51\tau_{CH2} + 24\omega_{CH_2} + 12\gamma_{CH}$
a′	1210 w	1216 w	1220	=C-H in-plane bending	$71\beta_{CH} + 10\rho_{CH_2} + 12\delta_{CH_2}$
a′	1100 s	1084 w	1090	CC stretching	$69\nu_{CC} + 19\nu_{C=C}$
a′	1004 m	1005 s	1014	CC stretching	$70\nu_{CC} + 14\nu_{C-Cl} + 10\nu_{C=C}$
a″	887 m	—	869	=C-H out-of-plane bending	$44\gamma_{CH} + 19\tau_{CH_2} + 24\omega_{CH_2} + 10\gamma_{CC}$
a′	826 s	826 m	831	CH_2 rocking	$74\rho_{CH_2} + 20\delta_{CH_2}$
a′	780 s	783 m	786	CH_2 rocking	$69\rho_{CH_2} + 22\delta_{CH_2}$
a′	708 w	—	709	C-C in-plane bending	$74\beta_{CC} + 12\delta_{CH_2} + 10\rho_{CH_2}$
a′	669 s	670 m	675	C-Cl stretching	$69\nu_{C-Cl} + 14\nu_{CH_2} + 19\nu_{C=C}$
a′	622 m	619 m	617	C-C in-plane bending	$69\beta_{CC} + 11\beta_{CH_2} + 14\beta_{C-Cl}$
a″	580 w	576 m	577	C-C out-of-plane bending	$71\gamma_{CC} + 24\tau_{CH_2} + 12\gamma_{C-Cl}$
a′	485 w	477 m	481	C-Cl in-plane bending	$54\beta_{C-Cl} + 21\beta_{CH_2} + 12\beta_{CC}$
a″	409 w	407 vw	411	C-C out-of-plane bending	$64\gamma_{CC} + 10\gamma_{C-Cl} + 18\tau_{CH_2}$
a″	—	343 w	333	C-Cl out-of-plane bending	$50\gamma_{C-Cl} + 31\omega_{CH_2}$
a″	—	152 w	134	C-C torsion	$47\tau_{CC} + 31\gamma_{CC} + 19\gamma_{CH}$
	—	125 vw	—	Lattice vibration	
	—	115 vw	—	Lattice vibration	

[a] vs, very strong; s, strong; m, medium; w, weak; vw, very weak; ν, stretching; δ, deformation; β, in-plane bending; γ, out-of-plane bending; τ, twisting/torsion; ω, wagging; and ρ, rocking.

The Raman spectrum is particularly rich in the lower frequency range, where there is little absorbance in the IR spectrum. In the Raman spectrum, the bands seen at 619 and 622 cm^{-1} in the infrared are assigned to the C−C in-plane bending modes. Similarly, the medium intensity bands observed at 576 and 407 cm^{-1} are attributed to C−C out-of-plane bending vibrations. The weak band observed at 152 cm^{-1} in Raman is assigned to the C−C torsional mode. The lower frequency bands normally overlap with other resonances, which makes them difficult to analyse into their individual vibrational components.

Potential Energy Distribution

To check whether the chosen set of assignments contributes the most to the potential energy associated with normal coordinates of the molecules, the PED has been calculated using the relation

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

where PED is the contribution of the ith symmetry coordinate to the potential energy of the vibrations whose frequency is ν_k, F_{ii} is the force constant evaluated by the damped least-square technique, L_{ik} is the normalised amplitude of the associated element (i, k) and λ_k the eigen value corresponding to the vibrational frequency $k(\lambda_k = 4\pi^2 c^2 \nu_k^2)$. The PED contributions, corresponding to each of the observed frequencies are listed in the table.

Conclusion

It is therefore clear that FTIR and FT-Raman spectroscopic studies have considerable potential for the complete analysis of the normal vibrations occuring in trans-1,4-polychloroprene. The results of normal coordinate analysis have been discussed. For all the fundamentals, there is close agreement between the observed and the calculated frequencies, and we have been able to satisfactorily assign the normal modes with confidence. The potential energy distribution contributions to each of the observed frequencies show the precision and reliability of the spectral analysis.

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