報　文

ポリ塩化ビニールの分子形態（英文）

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ポリ塩化ビニールの分子形態

ポリ塩化ビニールの分子構造は今迄数多く報告されているが、いまだにその部分的なものしか解決されていない。そこで塩素を含む炭化水素の可能な分子構造、即ち幾何学的な配位を考慮し、6種類のConformationを考え出し、その各々の構造について分子振動計算を試みた。その結果、ポリ塩化ビニールの構造中にはSyndiotacticのT-T-T-T型（結晶性）に帰属されるc-cl振動は602,640cm^{-1}に、Syndiotactic, 2fold,helix,T-T-G-G型は622,651,707cn^{-1}に、isotactic,threefold helix,T-G-T-G型は646,700cn^{-1}にそれぞれ吸収を示す。そしてすべてのポリ塩化ビニールは3つの型が共存し、その比率は製法に依存している。

CONFORMATIONS OF POLYVINYLCHLORIDE

Molecular vibration calculations can sometimes be useful in determining the structure of a molecule. Ideally, vibrational calculations are made for what are believed to be the possible structures of the molecule, the calculated frequencies are compared with the observed infrared spectrum, and this sometims allows one to rule out certain possibilities, or even permits the exact determination of the structure. The frequencies to be expected from a proposed structure depend upon the masses of the nuclei, the relative positions of the nuclei, and the vibrational force field of the molecule, that is, the stiffness of the"spring" connecting the nuclei・

The nuclear masses and positions of the proposed structure are known exactly. However, knowledge of the force field is usually very hard to come by. The conformational structure of polyvinylchloride was the object of the investigation. That is, the chemical formula of the polymer was known as ﹣(CHCL-CH$_2$-)n, the bond lengths and bond angles were known fairly accurately, but it was not known whether the polymer was completely straight, or helical,or what sort of bonds occurred in the chain like the chlorinated rubber which is imported recently.

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It is necessary to introduce a notation to describe the conformation of the molecule near one of the chlorine atoms.

It was assumed that there are the three usual stable rotational positions about each carbon-carbon bond.

Fig.1 shows the six possible conformations near a chlorine atom.The conformations are labelled S_{HH},$S_{HH'}$,etc.S stands for secondary,and subscript names the two atoms which are trans to the chlorine,(ref.1.2).But,there are probably not the exact conformations which occur in the actual molecules.

The problem of molecular conformations is difficult and is still only partially solved.

Approximate calculations for paraffins shows that the three stable rotational positions may be much as 10 to 15 degrees away from the standard positions, with a chlorine present there may be even more distortion, so that the tortion angles in the structures pictured are possibly inaccurate by about 5 or 10 degrees.

A force field which has been determined by fitting the calculated frequencies of such "known" structures to observed frequencies is affected to some extent by these inaccuracies.

The parts of the infrared spectrum that were used the most,and that will receive the most attention here,and the absorptions arising from the stretching of carbon-chlorine bonds.

These occur roughly in the region 550 to 750 cm^{-1}.

These absorption bands are usually strong,and their frequencies are very sensitive to changes in the molecular conformation near the chlorines,namely, the C-C1 stretching vibration is very sensitive to the conformation of the C-C chain,and it should be observed that the skeltal vibrations should be particularly sensitive to the rotational conformation of the C-C skelton,so they were by for the most useful features of the spectra.

From previous infrared studies,(ref.1),it was possible to make a reliable empirical assignment of stretching frequencies for single isolated carbon-chlorine bonds in different conformations.

The frequencies of the c'omformations are listed in Fig.1.

These carbon chlorine vibrations are not interacting with other carbon-chlorine vibrations,either because there is only one chlorine in the molecule,or the chlorines are widely separated.

This assignment is the basis for the whole vibrational analysis. At the beginning of this work,the reason for the dependence of the carbon-chlorine frequency upon the conformation had to be found. The presence of the two isotopes of chlorine does not an account for the range of frequencies observed.

The frequency of a pure carbon-chlorine stretching frequency decreases by about 8-9cm when a chlorine of mass 37 is substituted for a chlorine of mass 35.

Calculations for two forms of 2,4-dichloropentane show that actual frequency shifts to be expected are about 4 to 6cm.

The isotope of mass 37 is one third as common as the other,so its contribution to the spectrum should be correspondingly weaker.

It has to be kept in mind,however,as a likely cause of some of the irregularities observed in the absorption peaks assigned to carbon-chlorine stretching.

The real problem in explaining the variation of the carbon-chlorine frequencies with conformation was to find the force field involved.

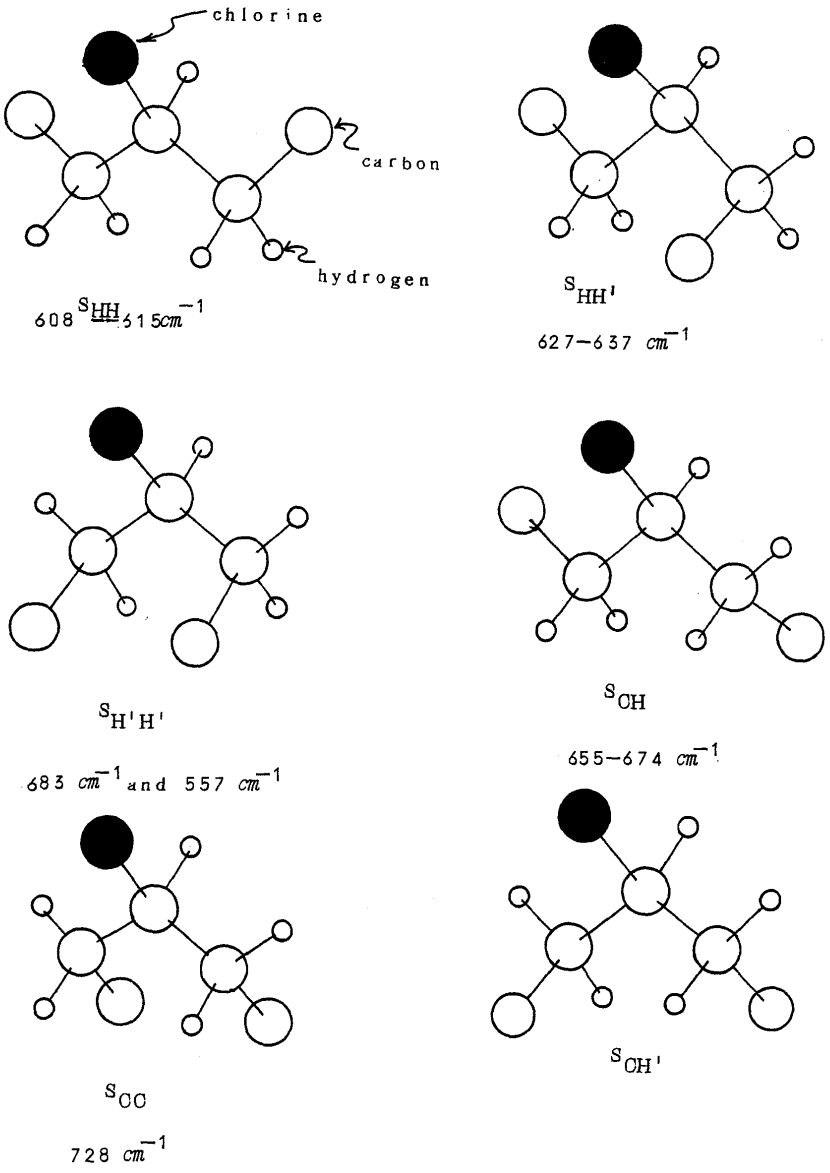


Fig 1

Figure 1 Secondary chloride conformations and empiricalty determined Carbon-chlorine stretching frequencies.

Torsion coordinates were not included because calculations for 2-chloropropane showed that there was very little interaction between the torsion vibration and the carbon-chlorine stretching.

Polyvinylchloride has the chemical repeat unit CHC1-CH_2,from chemical evidence (ref.3),we know that it has a head-to-tail structure (ref.12),and from X-ray evidence (ref.4).

So it seems that most of the tiime during polymerization,successive chlorine atoms are placed on opposite sides of the carbon back-bone.(when successive chlorines are placed on opposite sides of the carbon back-bone the polymer is called syndiotactic,when all the chlorines are placed on the same side the polymer is called isotactic).

Fig.2 is a picture of the extended syndiotactic PVC1,this is probably the predominant structure in the material.

There are two other plausible structures for polyvinylchloride.

Fig.3 shows a folded syndiotactic structure.

Syndiotactic polyproprlene can take this form (ref.5),so it is worth considering for syndiotactic polyvinylchloride.

If polyvinylchloride contained some segments with an isotactic placement of chlorine these segments would be expected to curl up into helices because of the repulsion between chlorine atoms.

This is what happens to isotactic polyproprlene (ref.6).

Fig.4 is a picture of the helical isotactic polyvinylchroride structure modelled after isotactic polypropylene,with three units in one turn (see Fig,5C).

This is only a conjecture,the actual helix could be looser,say with seven units in two turns.

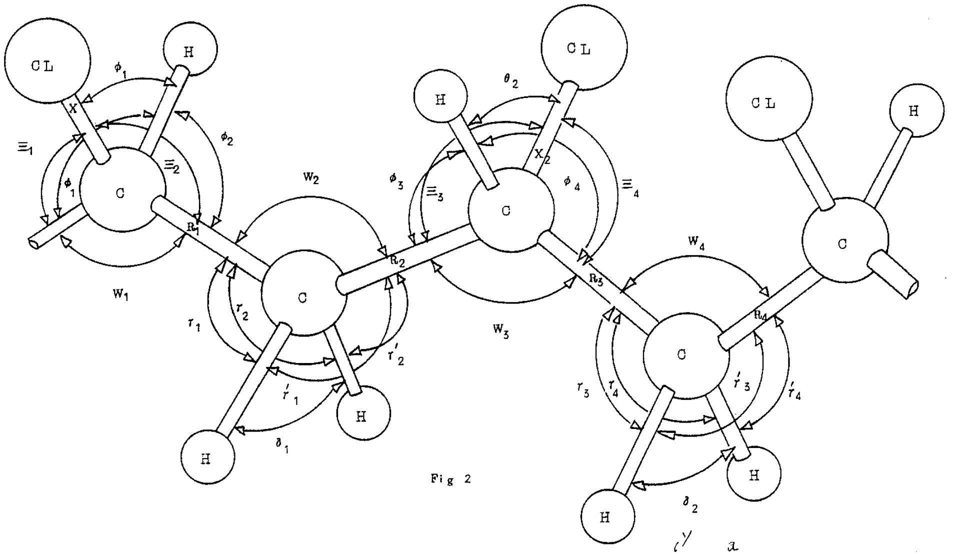
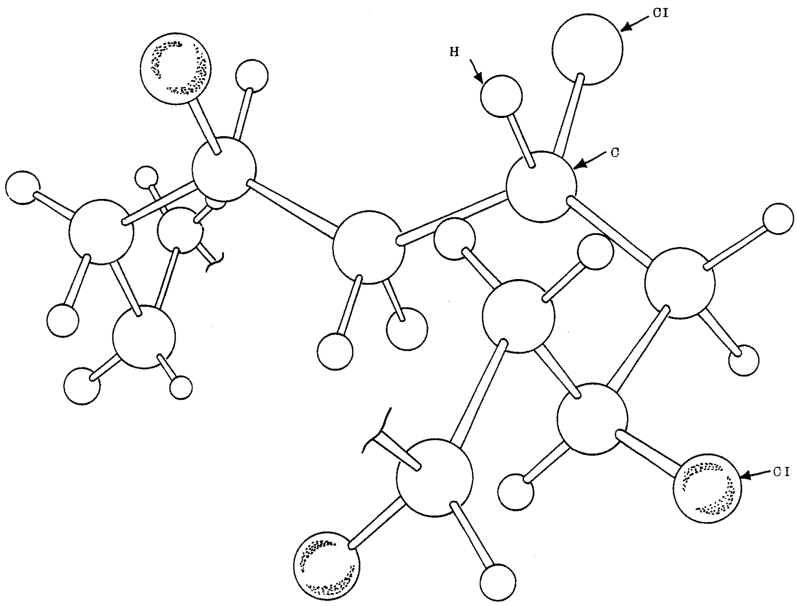


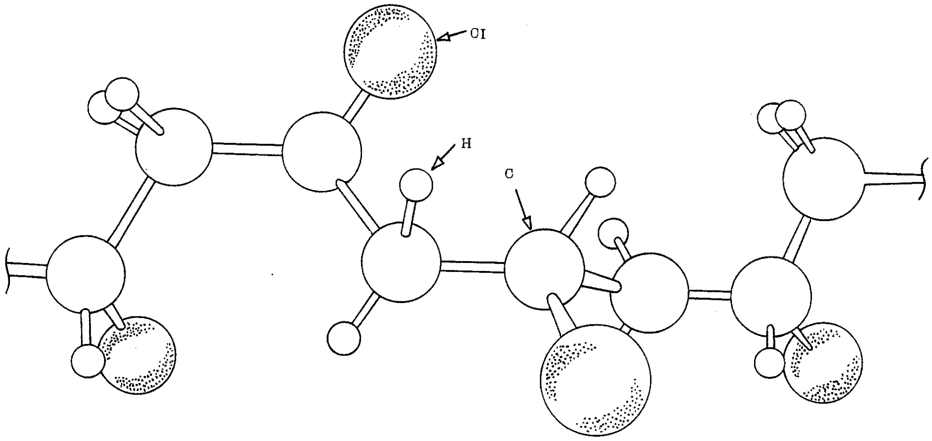
Fig 2

Figure 2 structure and Intermal Coordinates of Extended Syndiotactic polyvinylchloride



SYNDIOTACTIC POLY (VINYLCHLORIDE):2-FOLD HELIX-TTGG

Figure 3 Folded Syndiotactic polyvinylchloride



ISOTACTIC POLY (VINYLCHLORIDE): THREE-FOLD HELIX-TG

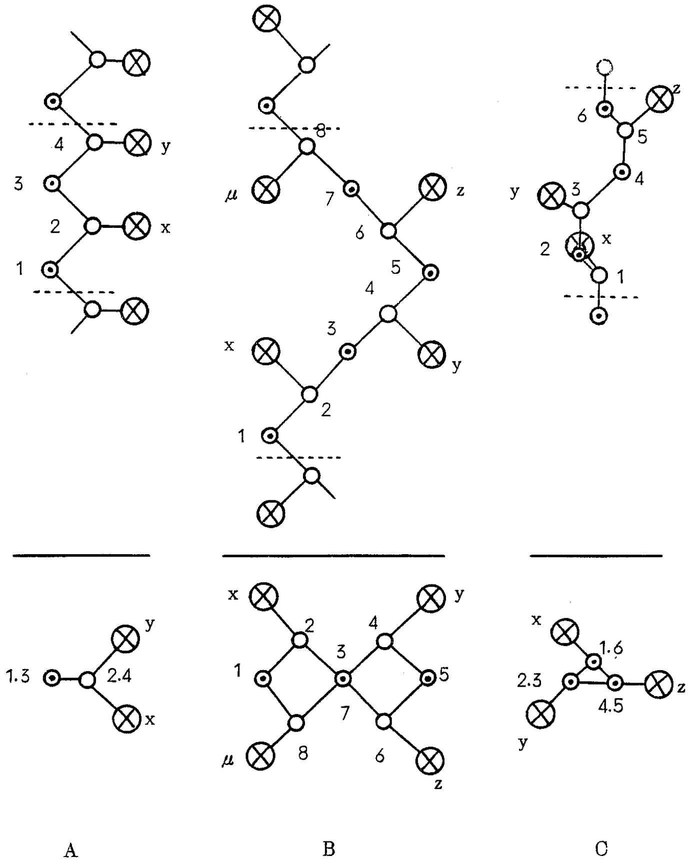
Figure 4 Helical isotactic polyvinylchoride

The polyvinychroride spectrum contains several bands in the carbon chlorine stretching region.

The spectrum changes quite drastically with changes in the conditions under the sample in prepared.Fig.6 shows the spectra of samples prepared in different ways.

Table 1 listed the observed carbon-chlorine frequencies,their empirical assignment to the crystalline and amorphous phases (ref.7,8) and the calculated frequencies for the three polyvinylchloride structure. As you can see that normal polyvinylchloride is not a stereoregular polymer and presents itself as an atactic polymer with primary syndiotactic conformations of parts of the chain (ref.13,14). The calculation confirms the assignment of the 602cm and 640cm bands to the foundamental C-C1 vibrations of the long regular syndiotactic parts of the chain. We propose that the wide bands at 615cm,which lies between 640cm and 602cm, is connected with C-C1 vibrations in the short,planear,syndiotactic parts in the amorphous regions of the polymer.

Fig 5



A Extended syndiotactic structure (All-Trans)

B Folded syndiotactic Structure (T-T-G-G)

C Threefold isotactic helix (T-G-T-G)

The increase in the intensity of this band in comparison with the 690 band on elongated of a film of PVC also indicates that this band belongs to the elongated part of the chain (ref.10).

There is little evidence that the frequencies of the other two forms are present in the observed spectra,so according to the calculation,there are no long folded syndiotactic or helical isotactic chains present in polyvinylchloride.

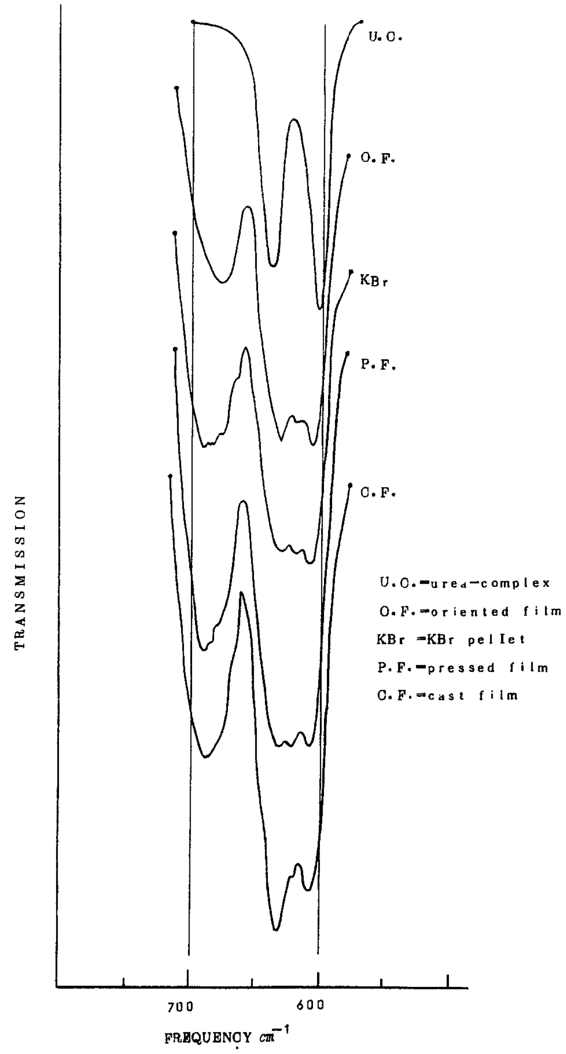


Fig 6

TABLE 1

Observed and Calculated Carbon-chlorine Frequencies for Polyvinylchloride.

Observed Frequency and intensity		Phase	Calculated Frequencies Syndiotactic Extended	 Syndiotactic Folded	 Helical isotactic
602	S	Crystalline	607		
612	S	Amorphous			
622	W	〃		622	
640	S	Crystalline	634		
				651	646
685	W	Amorphous			
693	S	〃			
				707	700
750	W	Amorphous			

As we can see that most of polymer vibrational spectra have concentrated on geometrically regular,chemically homogeneous structure.However,most polymers contain many irregularities,one of these is a conformational irregularity,that is,a bend or twist in the PVC chain.

Table 2 lists the calculated frequencies and potential energy distributions and observed frequencies for extended syndiotactic PVC.(the symmetry coordinates for the extended syndiotactic form are listed in table 5, more details of the calculations for the helical isotactic and the folded syndiotactic forms are given in table 3 and 4.

Table 5.
Symmetry Coordinates for Extended Syndiotactic P.V.C (C2V Symmetry)

Class A_1 Coordinates

$R = R_1 + R_2 + R_3 + R_4$

$X = X_1 + X_2$

$W = W_1 + W_3$

$CCC = W_2 + W_4$

$\theta = \theta_1 + \theta_2$

$\delta = \delta_1 + \delta_2$

$r = r_1 + r_2 + r_3 + r_4 + r'_1 + r'_2 + r'_3 + r'_4$

$t = r_1 - r_2 - r'_1 + r'_2 - r_3 + r_4 + r'_3 - r'_4$

$\phi = \phi_1 + \phi_2 + \phi_3 + \phi_4$

$\Xi = \Xi_1 + \Xi_2 + \Xi_3 + \Xi_4$

Class B_1 Coordinates

$R = R_1 - R_2 - R_3 + R_4$

$X = X_1 - X_2$

$W = W_1 - W_3$

$\theta = \theta_1 - \theta_2$

$w = r_1 + r_2 - r'_1 - r'_2 - r_3 - r_4 + r'_3 + r'_4$

$r = r_1 - r_2 + r'_1 - r'_2 + r_3 - r_4 + r'_3 - r'_4$

$\phi = \phi_1 + \phi_2 - \phi_3 - \phi_4$

$\Xi = \Xi_1 + \Xi_2 - \Xi_3 - \Xi_4$

Class B_2 Coordinates

$R = R_1 - R_2 + R_3 - R_4$

$w = r_1 + r_2 - r'_1 - r'_2 + r_3 + r_4 - r'_3 - r'_4$

$r = r_1 + r_2 + r^{2}_{1} - r'_2 - r_3 + r_4 - r'_3 + r'_4$

$\phi = \phi_1 - \phi_2 - \phi_3 - \phi_4$

$\Xi = \Xi_1 - \Xi_2 + \Xi_3 - \Xi_4$

Class A_2 Coordinates)
(infrared inactive)

B_2 Vibrations absorb light which is polarized parallel to the chain axis.

A_1 and B_1 Vibrations absorb light which is perpendicular to the chain axis.

TABLE 2

Calculated and Observed Frequencies for Extended Syndiotactic Polyvinylchloride (600cm^{-1} 1000cm^{-1})

Observed		Calculated		Potentrial Energy
602	VS	607	B_1	X(75)
640	S	634	A_1	X(74)
830	m	833	B_2	(78)＋(14)
962	m	982	B_1	(41)-R(37)

TABLE 3

Helical Isotactic PVC (C_3 Symmetry)

Frequency		Potential Energy Distribution	
646	A	X(65)	R(15)
700	E	X(57)	CCC(11)
848	A	(62)	(17)
892	E	(33)	R(36)
978	A	R(53)	W(12)

Class A vibrations will have a dipol parallel to the chain,and class E vibrations will have a dipole perpendicular to the chain.

TABLE 4

Folded Syndiotactic P.V.C.(D_2 Symmetry)

Frequency		Potential Energy Distribution
622	B_1	X(75)
651	B_2	X(74)
707	B_3	X(52)

(762)	A	X(52),	W(12)	
796	B_2	(49),	R(26)	
852	B_1	(65),	(18)	
916	B_3	R(38),	(38),	X(12)
927	B_1	R(46),	(29)	

Class A vibrations are infrared inactive,
Class B vibrations have polarizations parallel to the chain,and
Class B_2 and Class B_3 vibrations have polarizations perpendicular to the chain.

Investigation of irregularities in the structure of PVC.

1 Urea-complex PVC

The urea complex technique produces PVC with the regular extended syndiotactic structure illustrated in Fig.2.

When the material is pressed the structure presumably is destorted and the infrared spectrum changes.

Upon pressing,the 640cm peak becomes stronger and some what thicker,and a broad band around 680-690cm^{-1} appears.

Upon annealing of the sample a weak absorption appears at 750cm.

These changes presumably result from the defects of irregularities in the polyvinylchroride structure.

When extended syndiotactic PVC is distorted the chains are bent.

The bends in the chain can be regarded as defects.

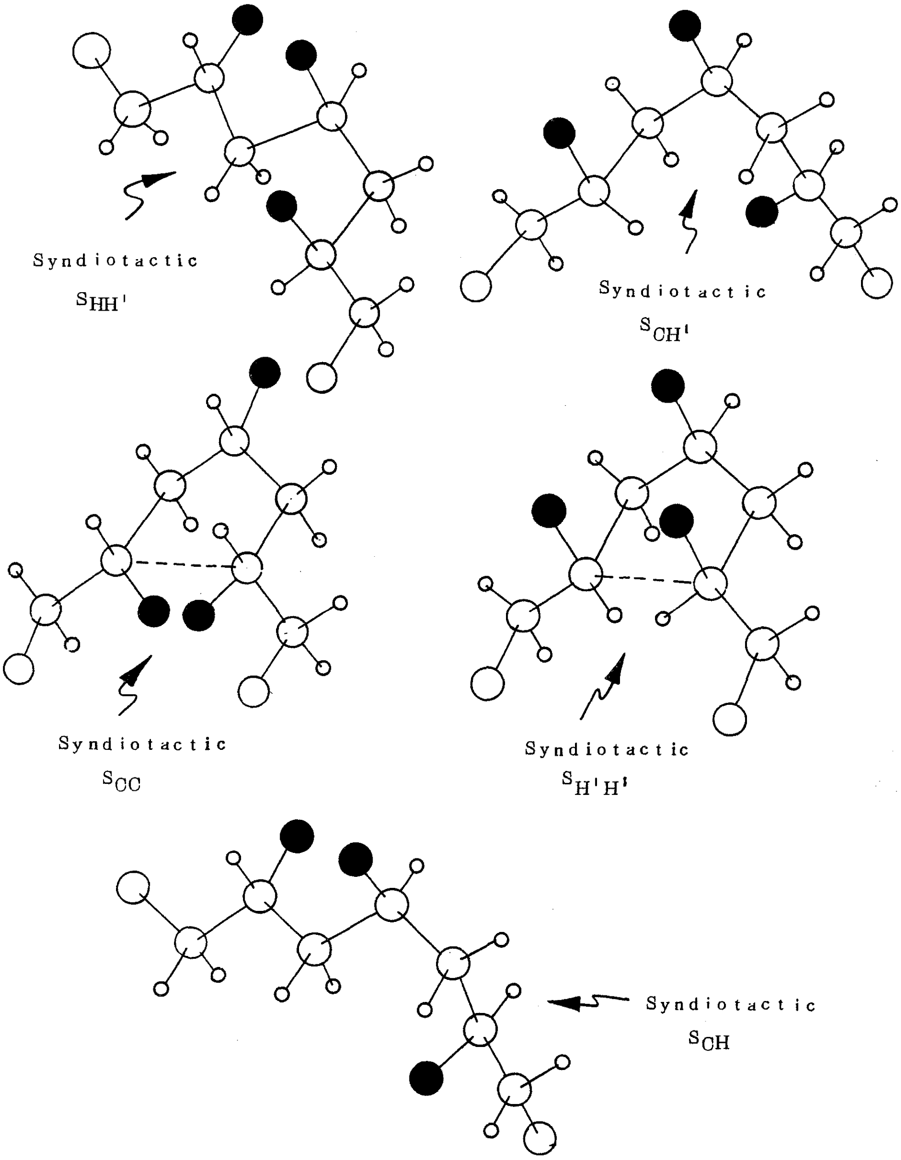
If we have a twist about one bond in the extended PVC chain,there are two possible structures at the bend.These are illustrated by the syndiotactic$S_{HH'}$ and S_{CH} polymer fragment in Fig.7.

We know that the S_{CH} carbon-chlorine stretching frequency is around 670cm^{-1}.

The calculation for syndiotactic S_{CH} fragment gives 692cm^{-1},as the S_{CH} defect frequency.

It seems almost certain that this structure,or something very similar to it, is introduced into the urea complex material by pressing.

The other possible structure contains an $S_{HH'}$ carbon-chlorine bond.
The isolated $S_{HH'}$ frequency is around 620 to 630cm^{-1}.



Syndiotactic $S_{HH'}$

Syndiotactic $S_{CH'}$

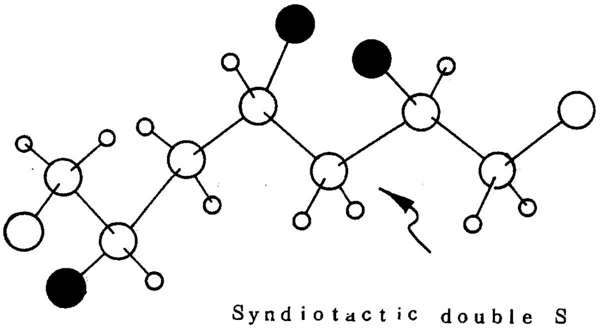
Syndiotactic S_{CC}

Syndiotactic $S_{H'H'}$

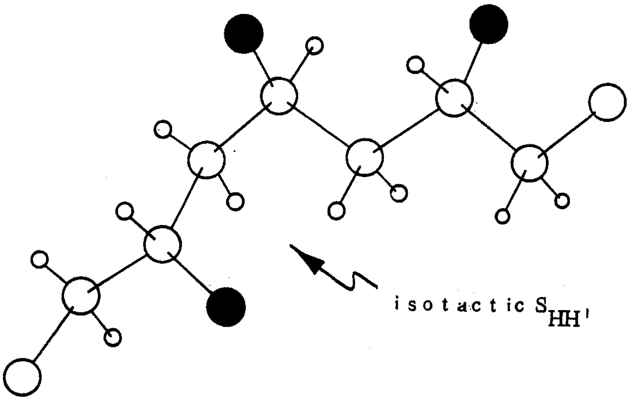
Syndiotactic S_{CH}

Fig 7

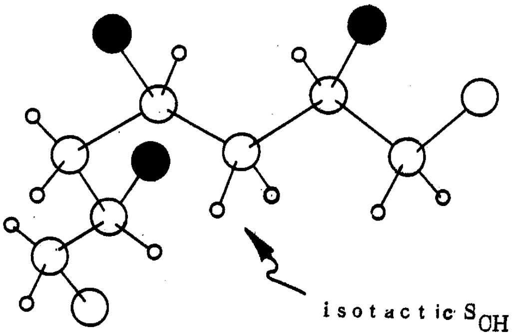
P.V.C. Fragments



Syndiotactic double S_{CH}



isotactic $S_{HH'}$



isotactic S_{OH}

Fig 7

The vibrational calculation for the syndiotactic $S_{HH'}$ fragment gives 638cm as the $S_{HH'}$ defect frequency.

But,it is impossible yet to say whether or not $S_{HH'}$ defects exist in polyvinyl-chroride.

If we allow torsions about two adjacement bonds we get three new structures invovling $S_{H'H'}$,and S_{CC} chlorines.

Calculations were done for the corresponding fragments,labelled these syndiotactic $S_{H'H'}$,$S_{CH'}$ and S_{CC} in Fig.7.

All of these predicted out side-of-band frequencies 605,687 and 749cm, respectively.

The $S_{CH'}$ conformation,with a frequency at 687,is probably present.The S_{CC} is hard,though,to take these structures seriously because of the small carbon-carbon distances indicated in Fig.7 by dish lines.

A more likely explanation of the 750cm absorption is that it comes from a double S_{CH} structure similar to the one in Fig.7.

2 Non-urea-complex PVC.

PVC,that is,is not made by urea complex technique has a much less regular structure than urea-complex-PVC,ordinary PVC is not as crystalline,and there are some isotactically placed chrorine atoms.

It is spectrum is similar to that of pressed urea-complex PVC,with the addition of a band,sometimes quite strong,at about 615cm.The 615cm peak is the dominant band in the spectrum of dissolved PVC,so it seems most reasonable to assign this to completely amorphous regions in the solid material.

Table 6 summarizes the assignments of the major bands in the PVC spectra.

Table 6 Assignment of the PVC carbon-chlorine stretching frequencies-urea-complex PVC.

602
640 crystalline extended syndiotactic phase
pressed urea-complex PVC
602

640	crystalline extended syndiotactic phase
690	S_{CH} and $S_{CH'}$ bends
750	double S_{CH} structures

non-urea-complex PVC

602	crystalline extended syndiotactic phase, isotactic S_{HH} bends(?).
612	amorphous phase
622	"isolated" S_{HH} chlorine atoms?
640	extended syndiotactic crystalline phase
690	S_{CH} and $S_{CH'}$ bends
750	double S_{CH} structure.

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