

Stable Conformations of 1,4-Polybutadiene Chains and Their Model Compound Molecules

Takehiko SHIMANOUCI, Yasuaki ABE, Yasuhide ALAKI

*Department of Chemistry, Faculty of Science, University of Tokyo,
Hongo, Tokyo, Japan.*

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ABSTRACT: Rotational isomerism in model compounds of *cis*- and *trans*-1,4-polybutadienes was studied. Infrared spectra in the region 600—300 cm^{-1} were measured for *cis*- and *trans*-2-butenes, 1-butene, 1-pentene, 1-hexene, *cis*- and *trans*-2-pentenes, *cis*- and *trans*-4-methyl-2-pentenes, *cis*- and *trans*-3-hexenes, *cis*-2-hexene, and 1,5-hexadiene. Normal frequencies were calculated for the low frequency vibrations of rotational isomers. From changes in the spectra in the gaseous, liquid, and solid states, it was concluded that the *cis* and *skew* conformations are stable for C—C bond neighbouring the *trans* C=C bond, and only the skew conformation is stable for the C—C bond neighbouring the *cis* C=C bond.

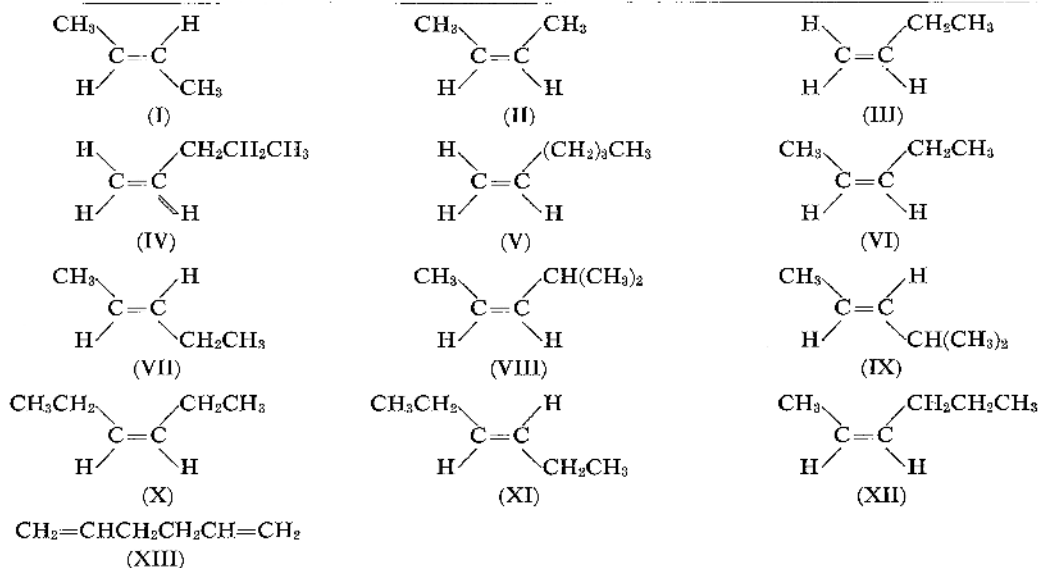
The stable conformations of *cis*- and *trans*-1,4-polybutadiene chains are discussed, taking into account the infrared spectra of these polymers and the stable conformations of the model compound molecules.

KEY WORDS Polybutadiene / Model Compound / Infrared Spectra /
Raman Spectra / Conformation / Rotational Isomer / Normal Vibration /
Force Constant /

In a previous paper the rotational isomerism of methylbutenes and methylpentenes was studied and the stable conformations of *cis*- and *trans*-1,4-polyisoprenes were discussed.¹ In the present

paper the same method is applied to *cis*- and *trans*-1,4-polybutadienes and the rotational isomerism of the molecules shown in Table I is dealt with.

Table I. Model compounds studied



These molecules have skeletal deformation vibrations in the region 600–300 cm^{-1} , the frequencies of which are sensitive to conformation. The spectra in this region were accordingly measured in the gaseous, liquid, and solid states and rotational isomerism was studied from the variations in these spectra.

EXPERIMENTAL

1-Butene, 1-pentene, 1-hexene, 2-pentene, 2-hexene, and *cis*- and *trans*-2-butene were obtained commercially. The *cis* and *trans* compounds of 2-pentene and 2-hexene were produced by gas-chromatography separation. 1,5-Hexadiene, and *cis* and *trans* compounds of 4-methyl-2-pentene and 3-hexene were provided by Tokyo Kagaku Seiki Co. and were used without further purification. Analysis by gas-chromatography for all the compounds showed that the purity of the samples was higher than 99%. *Cis*- and *trans*-1,4-polybutadienes were provided by the Bridgestone Tire Company.

The infrared spectra were recorded with an Hitachi EPI-L double-beam grating spectrometer in the region 700–250 cm^{-1} , and with an Hitachi FIS-1 double beam grating spectrometer in the region 300–60 cm^{-1} . Spectra in the gaseous state were measured by using a 10-cm cell and those in the liquid state were measured with 0.025–1.0-mm cells, KBr, KRS-5 or polyethylene windows being used. To obtain solid state spectra, measurements were made at the temperature of liquid nitrogen; samples deposited on cooled KRS-5 or silicon windows were repeatedly annealed until no further spectral change was observed.

The polybutadiene films were obtained from benzene and carbon disulfide solutions.

The Raman spectra were measured at the temperature of liquid nitrogen and were obtained by using a method described previously.²

CALCULATION OF NORMAL VIBRATIONS

For the calculation of normal frequencies and their modes, a HITACHI 5020E computer in the Computer Centre of the University of Tokyo, and programs BGLZ and LSMB prepared in our laboratory were used.³ All the stretching vibra-

tions were factored out by the high-frequency splitting technique.

First the calculation was made for *trans*-2-butene, the modified UBFF being assumed and the force constants being transferred from small molecules. The result was compared with the observed infrared and Raman bands and the force constants were adjusted by the least squares method.

Secondly the normal frequencies of *cis*-2-butene, and the *cis* and *skew* forms^{1,4,5} of 1-butene, *cis*-2-pentene, and *trans*-2-pentene were calculated, the force constants obtained above being used. They were used for the assignments of the observed infrared and Raman spectra. The values of the force constants associated with the skeletal deformation vibrations were adjusted. The agreement between the observed and calculated frequencies was limited, unless other force constants referred to below were taken into account. The results for the low frequency vibrations are given in the column under "Calcd I" of Table II.

Next the final least squares adjustment was made for the force constants associated with the low-frequency bands of the above seven molecules, leaving the other constants unadjusted. The *cis* form of *cis*-2-pentene was excluded, since the bands for this form were not observed. In this calculation the repulsive force constants (R) for the two carbon atoms situated in the *cis* position, the interaction constant (WY) between the CH wagging and C—C torsional modes, and the interaction constant (WW) between the two neighbouring CH wagging modes were taken into account.

The force constants obtained are shown in Table III, where the definitions are given by

$$V = \sum \frac{1}{2} K_i (\Delta r_i)^2 + \sum \frac{1}{2} H_{ij} r_i^0 r_j^0 (\Delta \phi_{ij})^2 + \sum \frac{1}{2} F_{ij} (\Delta q_{ij})^2 + \sum \frac{1}{2} Y_i (\Delta t_i)^2 + \sum \frac{1}{2} W_{ijk} (\Delta \pi_{ijk})^2 + \text{terms due to the gem internal tension}$$

The parameters, r , ϕ , q , t , and π are the bond length, the bond angle, the distance between non-bonded atoms, the angle of internal rotation,⁶ and the out-of-plane displacement angle,⁷ respectively, r^0 being the equilibrium length. The values of F' appearing in the gem internal tension is assumed to be $-0.1F$.⁸ The structural

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 Table II. Low frequency vibrations of olefin molecules (cm⁻¹)

Molecule	Calcd I ^a	Calcd II	Obsd ^b	Assignments
<i>trans</i> -2-Butene	492	483	500	C=C-C def. (Ag)
	304	295	297	C=C-C def. (Bu)
	262	254	263	C-C torsion (Bu)
<i>cis</i> -2-Butene	610	597	587	C=C-C def. (B ₁)
	238	290	290	C=C-C def. (A ₁)
	666	670	678	=CH- wag. (B ₂)
	449	399	392	C=C torsion (A ₂)
1-Butene (<i>cis</i>)	566	582	557	CH ₂ twist. ^c
	562	544	540	C=C-C-C def.
	247	290	291	C=C-C-C def.
1-Butene (<i>skew</i>)	613	623	638	CH ₂ twist. ^c CCC def.
	441	431	433	C=C-C def.
	364	350	325	CCC def., =CH- wag.
<i>cis</i> -2-Pentene (<i>cis</i>)	640			C-C-C def., CH ₂ rock.
	418			C=C torsion
	346			CCC def., C-C-C def.
	151			C-C-C-C def.
<i>cis</i> -2-Pentene (<i>skew</i>)	712	690	694	CH ₂ twist. ^c
	583	586	570	C-C-C def.
	485	456	455	C=C torsion, CCC def.
	310	302	310	CCC def. C=C torsion
	243	278	265	C-C=C-C def.
<i>trans</i> -2-Pentene (<i>cis</i>)	574	558	576	C=C-C-C def.
	378	381	373	C-C=C def., CCC def.
<i>trans</i> -2-Pentene (<i>skew</i>)	497	485	488	C-C=C def., CCC def.
	414	402	415	CCC def., C=C-C def.
	302	297	305	C-C=C-C def.
<i>cis</i> -4-Methyl-2-pentene (<i>skew-skew</i>)		590	586	CC-CC def.
		479	500	CCC twist., C=C torsion
		422	420	CC wag., CC-C def.
		349	347	CCC scis., CC wag.
		272		CCC twist., CH ₃ torsion
<i>cis</i> -4-Methyl-2-pentene (<i>cis-skew</i>)		657		CC=CC def., =CCC def.
		483		CCC twist., C=C torsion
		387		CCC def.
		369		CCC scis.
		290		CCC def., CH ₃ torsion
<i>trans</i> -4-Methyl-2-pentene (<i>skew-skew</i>)		478	487	CC=C def., CCC scis.
		450	460	CCC wag., CC-C def.
		418	421	CCC twist.
		321	343	CCC scis., C=CC def.
		234		CH ₃ torsion, C=CC def.
		191		CH ₃ torsion, C-CC def.
<i>trans</i> -4-Methyl-2-pentene (<i>cis-skew</i>)		557	568	C=CCC def.
		423	438	CCC def., C-C torsion
		407	405	CCC def. CC=C def.
		344	328	CCC scis., CC-C def.
		223		CH ₃ torsion, C=CC def.
		191		CH ₃ torsion, C=CC def.

Table II. (Continued)

Molecule	Calcd I ^a	Calcd II	Obsd ^b	Assignments	
<i>cis</i> -3-Hexene (SS form)		576	564	C-CC def., -CCC def.	
		481	487	CCC def., C=C torsion	
		397	363	CCC def.	
		289		C=CC def., CH ₃ torsion	
		226		CCC def., CH wag.	
	(SS' form)		579	575	C-CC def., =CCC def.
			503	500	CCC def., C=C torsion
			362	345	CCC def.
			278		C-CC def., CH ₃ torsion
			259		CCC def., CH wag.
<i>trans</i> -3-Hexene (SS' form)		470	485	CCC def., C=CC def.	
		307	323	C=CC def., CH ₃ torsion	
	(SS form)		421	(405)	CCC def., C=CC def.
			381	(365)	CCC def., C-CC def.
	(CS form)		270	(276)	C=CC def., CH ₃ torsion
			561	567	C=CCC def.
			403	(405)	CCC def.
			374	(365)	C-CC def.
	(CC form)		273	(276)	CH ₃ , CC torsion, CH wag.
			496		C-CCC def.
		288		CH ₃ torsion, CH wag.	

^a Force constants used are $H(C=CC)=0.32$, $F(C=CC)=0.4$, $H(CCC)=0.32$, $F(CCC)=0.4$, $Y(C-C)=0.64$, and $W(-CH)=0.35$.

^b Frequencies observed in the solid state.

^c Coupled strongly with =CH- wagging vibration.

parameters adopted are the same as those given previously.¹

The values of R obtained for the *cis* C...C repulsion are reasonable as compared with the corresponding values of F . As shown in Table IV, they decrease as the C...C distances increase. We ignored the H...H and H...C repulsions for the methyl or methylene groups situated in the *cis* position, since they are less important in the study of skeletal vibrations.

The calculated frequencies are shown in the column under "Calcd II" of Table II. The differences between the observed and calculated frequencies for these seven molecules at times exceed 10 cm⁻¹. However, the accuracy is sufficiently high for the conformation to be discussed adequately. In Table II the frequencies calculated from these force constants are given for 4-methyl-2-pentene and 3-hexene. They were used in the conformation analysis and the assignments of the observed bands.

trans-2-BUTENE

This molecule (I in Table I) takes the C_{2h} symmetry and there is no problem in the conformation. The infrared spectra in the NaCl and KBr regions and the Raman spectra in the liquid state have already been reported.⁹⁻¹³ However, we need the assignments for the skeletal deformation vibrations for the present study and the far-infrared spectra and the Raman spectra in the solid state were measured. Details are shown in Figure 1.

The Raman band at 500 cm⁻¹ is assigned to the symmetrical C=C=C deformation vibration. The antisymmetrical C=C=C deformation and the C=C torsional vibrations are expected to appear in the far-infrared region. The spectrum in the gaseous state has a complex band near 254 cm⁻¹. In the solid state it becomes a doublet. The C=C=C deformation vibrations are assigned to the 297 cm⁻¹ peak and the C=C

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 Table III. Force constants of olefins (MUBFF)^a

$K(\text{C}=\text{C})$	7.42	
$K(\text{=C}\cdots\text{C})$	3.24	
$K(\text{---C}\cdots\text{C})$	2.40	
$K(\text{=CH})$	4.39	
$K(\text{---CH})$	4.23	
$H(\text{C}=\text{CC})$	0.287	(0.015)
$H(\text{=CCC})$	0.260	(0.028)
$H(\text{---CCC})$	0.25	
$H(\text{C}\cdots\text{CH})$	0.16	
$H(\text{CC}'\text{H})$	0.23	
$H(\text{C}'\text{CH})$	0.21	
$H(\text{CCH})$	0.23	
$H(\text{HCH})$	0.365	
$H(\text{HC}'\text{H})$	0.37	
$F(\text{C}\cdots\text{CC})$	0.40	
$F(\text{CCC})$	0.40	
$F(\text{---CCC})$	0.40	
$F(\text{C}\cdots\text{CH})$	0.45	
$F(\text{CC}'\text{H})$	0.51	
$F(\text{C}'\text{CH})$	0.38	
$F(\text{CCH})$	0.40	
$F(\text{HCH})$	0.21	
$F(\text{HC}'\text{H})$	0.21	
$W(\text{=CH})$	0.359	(0.011)
$W(\text{=CH}_2)$	0.30	
$Y(\text{C}\cdots\text{C})$	0.485	(0.043)
$Y(\text{---C}\cdots\text{C})$	0.1	
$Y(\text{---C}\cdots\text{C})$	0.08	
$Y(\text{---CH}_3)$	0.08	
$WW(\text{trans})$	-0.044	(0.017)
$WW(\text{cis})$	-0.005	(0.011)
WY	0.063	(0.014)
$R(\text{=C}\cdots\text{C}\cdots)$	0.169	
$R(\text{---C}\cdots\text{C}\cdots)$	0.203	

^a K , H , F , and R are given in $\text{md}/\text{\AA}$ and W , T , WW , and WY in $\text{md}\cdot\text{\AA}$, the values in parentheses denote statistical dispersion.

torsion to the 263 cm^{-1} peak, since the former is calculated to be higher in frequency than the latter. These frequencies were used for the calculation together with those assigned earlier.⁹⁻¹²

cis-2-BUTENE

This molecule (II in Table I) takes the C_{2v} symmetry and the infrared and Raman spectra have also been reported.⁹⁻¹² We measured the far-infrared and Raman spectra in the solid state. The results are shown in Figure 2.

The strong infrared band at 678 cm^{-1} is as-

 Table IV. Repulsion constants, F and R in $\text{md}/\text{\AA}$, and interatomic distances, r in \AA ^a

	$r(\text{C}^*\cdots\text{C}^*)$	$r(\text{H}\cdots\text{H})$	F or R
	2.53		0.4
	2.50		0.4
	3.07	1.83	0.203
	2.95	2.17	0.169
	2.51	1.33	

^a $r(\text{C}^*\cdots\text{C}^*)$ is the distance between the two carbon atoms denoted with an asterisk. $r(\text{H}\cdots\text{H})$ is the shortest distance between the hydrogen atoms attached to C^* .

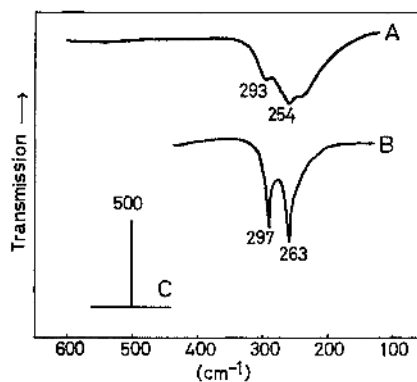


Figure 1. Infrared and Raman spectra of *trans*-2-butene: (A) gas, infrared; (B) solid, infrared; (C) solid, Raman.

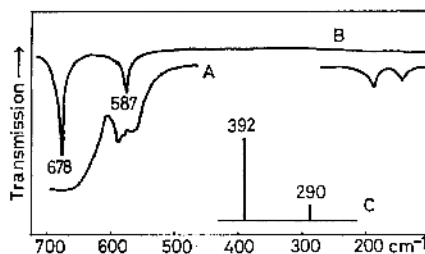


Figure 2. Infrared and Raman spectra of *cis*-2-butene: (A) gas, infrared; (B) solid, infrared; (C) solid, Raman.

signed to the symmetrical CH wagging vibration. The 587-cm^{-1} infrared and the 290-cm^{-1} Raman bands are assigned to the two C=C deformation vibrations. These assignments are supported by the frequency calculations. The remaining Raman band at 390-cm^{-1} is assigned to the C=C torsion. The frequencies given in "Calcd I" of Table II are somewhat different from those observed. This fact shows that the term due to the *cis* C...C repulsion is needed. For "Calcd II" where the repulsion is taken into account, agreement is closer.

1-BUTENE, 1-PENTENE, AND 1-HEXENE

The microwave spectra¹⁴ showed that the 1-butene molecule has two rotational isomers, *cis* and *skew*, in the gaseous state and that both isomers are almost equal in energy. The existence of isomers was also shown for the 1-olefins in the liquid state from the fact that their infrared spectra have two CH₂ twisting vibration bands near 550 and 640-cm^{-1} and that the former disappears in the solid state.¹⁵

The infrared spectra measured are shown in Figure 3. For 1-butene and 1-pentene the low-temperature spectra show that they are in the glassy state. We were unable to obtain the spectra in the crystalline state by means of the annealing procedure. For 1-hexene, however, repeated annealing led to crystallization and the spectrum shown in Figure 3 was obtained. The 557-cm^{-1} band disappeared, as reported previously.¹⁵ In addition it was observed the 312-cm^{-1} band also disappeared.

The fact that the CH₂ twisting vibration frequencies of the two rotational isomers are different may be explained from the coupling between the twisting vibration and the skeletal deformation vibrations. When the CH₂=CH—CH₂—CH₂ group takes the *cis* conformation, the CH₂ twisting mode does not couple with the skeletal deformation modes and gives a frequency near 550-cm^{-1} . When the group takes the *skew* conformation, the coupling occurs, the frequency becomes higher, and the band appears near 640-cm^{-1} .

This explanation is supported by the normal coordinate treatment for the *cis* and *skew* forms of 1-butene as shown in Table II. All the bands

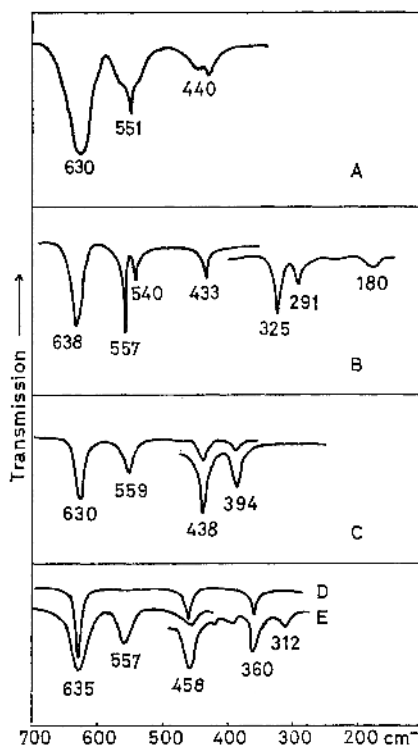


Figure 3. Infrared spectra of 1-olefins: (A) 1-butene, gas; (B) 1-butene, solid; (C) 1-pentene, solid; (D) 1-hexene, crystal; (E) 1-hexene, solid.

observed in the gaseous and solid states are reasonably assigned, as given in the table. The coexistence of the *cis* and *skew* forms is shown.

For the *cis* form the skeletal deformation vibration frequencies for "Calcd I" are somewhat different from those observed. The situation is similar to the case of *cis*-2-butene and the inclusion of the *cis* repulsion constant improves the situation, as shown in Table II.

For 1-butene the form remaining in the crystalline state is *skew*. The 1-pentene and 1-hexene molecules have the C—C axes other than that neighbouring the terminal vinyl group. Many rotational isomers are possible. In fact the two CH₂ twisting vibration bands near 550 and 640-cm^{-1} are not single bands, but they are overlaps of two or more. In the crystalline state they become sharp, showing that only one form remains. The information available is not sufficient to enable the isomer forms to be discussed in detail.

cis-2-PENTENE

The spectra in the liquid and solid states are given in Figure 4. The solid-state spectra show that the bands become sharp with repeated annealing; that no band disappears, and that the relative intensities of the observed bands show no appreciable change. Furthermore, the number of the observed bands is exactly as would be expected from one molecular form in this region. The existence of only one form is therefore concluded.

The frequencies of the observed bands are compared with those calculated for the *cis* and *skew* forms. As shown in Table II, the result is explained by the existence of the *skew* form. The agreement between the observed frequencies and "Calcd I" is close except for the lowest frequency deformation vibration. The situation is improved when the *cis* repulsion constant is taken into account. "Calcd II" shows the results.

This conclusion is supported by the energy of conformation. The two methyl groups are too close to each other for the *cis* form to be stable.

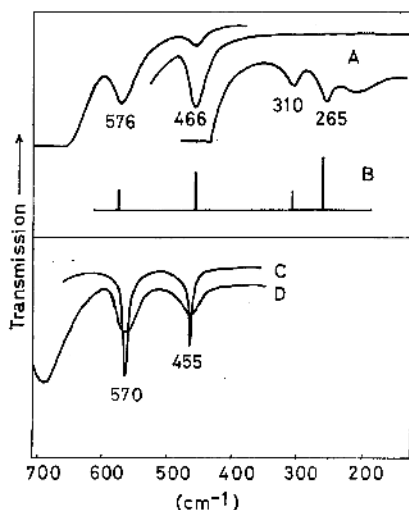


Figure 4. Infrared and Raman spectra of *cis*-2-pentene: (A) liquid, infrared; (B) liquid, Raman; (C) crystal, infrared; (D) solid, infrared.

trans-2-PENTENE

The spectra are shown in Figure 5. The number of bands observed in the liquid state

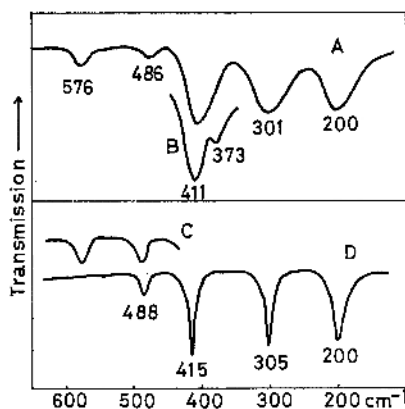


Figure 5. Infrared spectra of *trans*-2-pentene: (A) liquid at room temperature; (B) liquid at low temperature; (C) solid, glassy state; (D) crystalline state.

is larger than that expected for one form. The relative intensities of the bands, for example those at 576 and 486 cm^{-1} , in the liquid state vary with changes in temperature. In the solid state two bands at 576 and 373 cm^{-1} disappear. This demonstrates that the two forms coexist in the liquid state.

The frequencies of the observed bands were compared with those calculated for the *cis* and *skew* forms. The results are shown in Table II. The bands remaining in the solid states are assigned to the vibrations of the *skew* form. Those disappearing on solidifying are assigned to the vibrations of the *cis* form.

The change in relative intensities of the two bands at 576 and 486 cm^{-1} due to the temperature variation shows that the *skew* form is slightly more stable than the *cis* form in the liquid state. The fact that the *skew*-form bands are stronger than the *cis*-form bands is ascribed to the difference in the statistical weight, the value of the *skew* form being twice of that of the *cis* form.

In contrast to the fact that the methyl group repulsion makes the *cis* form of the *cis*-2-pentene molecule unstable, the two methyl groups of the *trans*-2-pentene molecule are far apart even for the *cis* conformation. This is the reason why the *cis* form is as stable as the *skew* form for this molecule.

cis-4-METHYL-2-PENTENE

Cis- and *trans*-4-methyl-2-pentene (VIII and IX in Table I) are not directly related to the structure of the polybutadiene chain. However, we include these two compounds because the method adopted in the present study can be checked from the conformation analysis of these molecules.

The methyl group repulsion discussed for the previous two compounds makes the *cis-skew*

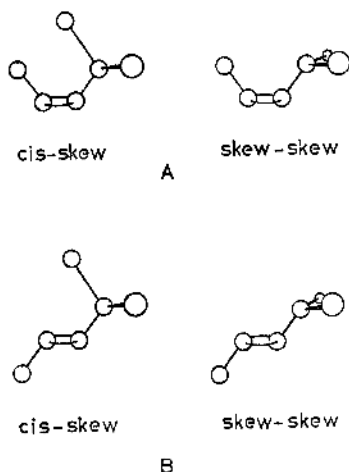


Figure 6. Rotational isomers of *cis*-4-methyl-2-pentene (A) and *trans*-4-methyl-2-pentene (B).

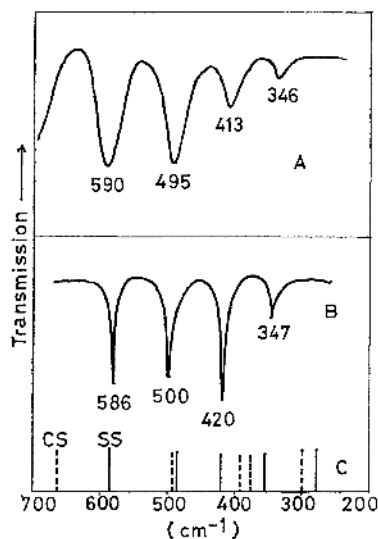


Figure 7. Infrared spectra of *cis*-4-methyl-2-pentene: (A) liquid; (B) crystal; (C) Calcd II.

form of the *cis*-4-methyl-2-pentene unstable. Therefore, only the *skew-skew* form is expected to exist for this molecule (see Figure 6). The infrared spectra shown in Figure 7 indicate that this is the case. The "Calcd II" values for the *cis-skew* form (CS) and the *skew-skew* form (SS) are given in Figure 7. The results clearly show that only the skew-skew form exists in the liquid and solid states.

trans-4-METHYL-2-PENTENE

The preceding discussions and the methyl group distance shown in Figure 6 suggest that the two rotational isomers, *cis-skew* and *skew-skew* in Figure 6, coexist for this molecule. The infrared spectra shown in Figure 8 show that this is the case. The "Calcd II" frequencies for the *cis-skew* (CS) and *skew-skew* (SS) forms are also given in Figure 8. The bands appearing in the liquid, amorphous solid, and crystalline states are assigned to the vibrational modes of the *skew-skew* form and those appearing in the

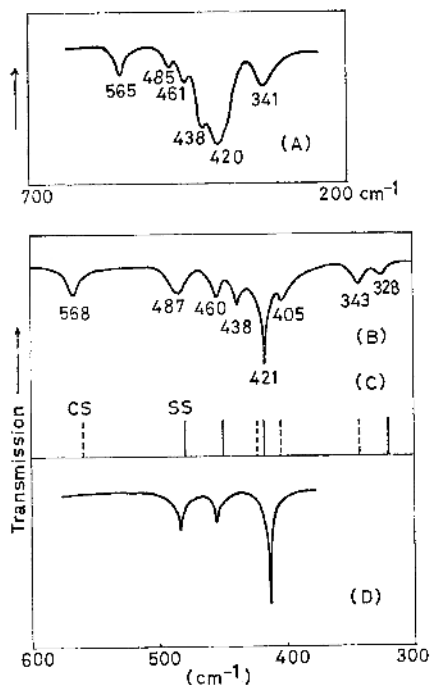


Figure 8. Infrared spectra of *trans*-4-methyl-2-pentene: (A) liquid; (B) amorphous solid; (C) Calcd II; (D) crystal.

liquid and amorphous states and disappearing in the crystalline state are assigned to the modes of the *cis-skew* forms.

cis-3-HEXENE

Cis- and *trans*-3-hexenes (X and XI in Table I) are important model compounds of *cis*- and *trans*-1,4-polybutadienes. For *cis*-3-hexene the *cis* conformation of the terminal ethyl group is now rejected and the possible conformations are SCS and SCS' given in Figure 9.

The infrared spectra are shown in Figure 10. The bands near 580, 490, and 350 cm^{-1} are doublets in the liquid and amorphous solid states. By repeating the annealing procedure we obtain the spectrum in the crystalline state, in which the above three doublets become three sharp bands, although the last band accompanies a shoulder.

The above results show that the two isomers, SCS and SCS', exist in the liquid and amorphous solid states and only one of them remains in the crystalline state.

In Figure 10 the "Calcd II" frequencies are also shown. They suggest that the form in the

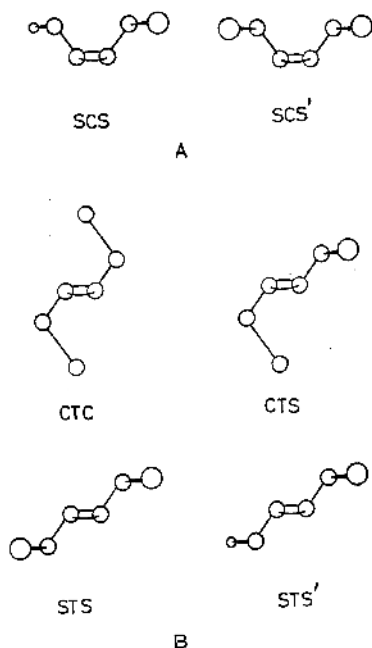


Figure 9. Rotational isomers of *cis*-3-hexene (A) and *trans*-3-hexene (B).

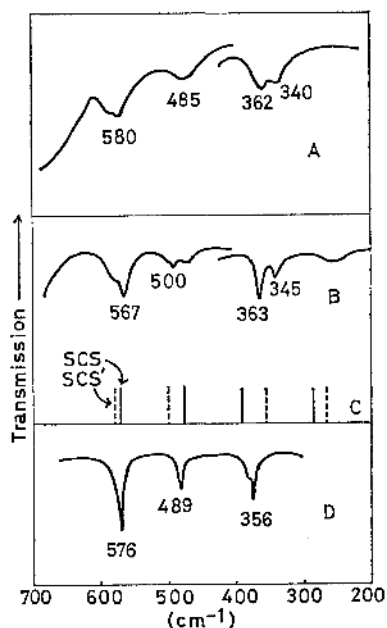


Figure 10. Infrared spectra of *cis*-3-hexene: (A) liquid; (B) solid; (C) Calcd II; (D) crystal.

crystalline state is probably SCS. The values of frequencies calculated however may not be sufficiently reliable to allow a valid conclusion to be drawn from this coincidence.

The changes in temperature do not alter the relative intensities of the infrared bands in the liquid state appreciably. This shows that the difference between the energies of the SCS and SCS' forms is very small.

trans-3-HEXENE

The preceding discussions suggest that the *trans*-3-hexene molecule takes CTC, CTS, STS, and STS' shown in Figure 9. The infrared spectra are given in Figure 11. The "Calcd II" frequencies are also given in the figure.

The properties and the estimated relative amounts of the four forms are in Table V. The CTC and STS' forms have a center of symmetry and the two skeletal deformation vibrations are infrared active. For CTS and STS the four skeletal deformation vibrations are infrared active. The estimated amount for the CTC form is smaller than those for the other three forms.

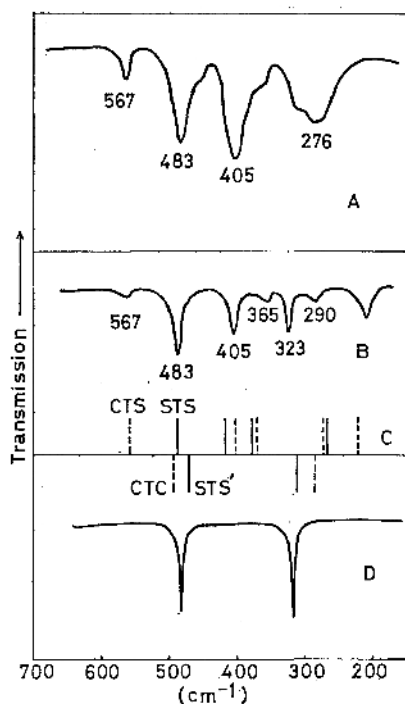


Figure 11. Infrared spectra of *trans*-3-hexene: (A) liquid; (B) solid; (C) Calcd II; (D) crystal.

Table V. The properties and the estimated relative amounts of the four forms of *trans*-3-hexene

	CTC	CTS	STS	STS'
Symmetry	C _{2h}	C ₁	C ₂	C _i
Relative amount for $\Delta E=0^a$	1	4	2	2
Relative amount for $\Delta E=-200$ cal/mol ^a	1	5.5	4	4
Number of infrared active skeletal deformation vibrations	2	4	4	2

^a The two possible values roughly estimated from the infrared spectra are used here in the discussion.

Figure 11 shows that the form remaining in the crystalline state is STS'. The two bands at 483 and 323 cm⁻¹ in the crystalline state are assigned to the two skeletal deformation vibrations of the STS' form, the frequencies of which are calculated as 470 and 307 cm⁻¹. These two bands are strong in the liquid and amorphous solid states. This fact is consistent with the estimated relative amounts given in Table V.

In addition to these two bands several bands appear in the liquid and amorphous solid states. They are ascribed to the bands of the CTS and STS forms. The bands due to the CTC form are not assigned. They may be too weak or overlapped by other bands.

After the present study had been completed, we were informed that Piaggio, Dellepiane, and Zerbi¹⁶ studied the infrared and Raman spectra of this compound, and compared the results with the result of the normal frequency calculation. They reached the same conclusion.

cis-2-HEXENE

This molecule (XII in Table I) has three possible conformations, CST, CSG, and CSG'; since the CC conformation is unstable and the axis of the CH—CH₂—CH₂—CH₃ group takes the *trans* and *gauche* conformations. The infrared spectra is shown in Figure 12.

The band near 460 cm⁻¹, which is similar to the 460 cm⁻¹ band of *cis*-2-pentene and is assigned to the C—C torsion, has a doublet structure in the liquid and amorphous solid states and becomes a sharp single band in the crystalline state. This indicates the existence of rotational isomers. However, the information available is too limited for the conformations to be discussed in any detail.

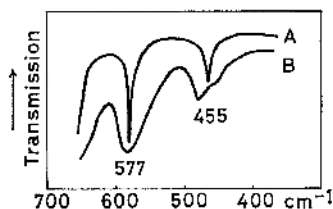


Figure 12. Infrared spectra of *cis*-2-hexene: (A) crystal; (B) liquid.

1,5-HEXADIENE

This molecule (XIII in Table I) has three C—C axes of internal rotation which are inserted between the two C=C bonds. It is one of the important model compounds of 1,4-polybutadiene. The molecule has possible conformations CTC, CGC, CTS, CGS, CGS', STS, SGS, SG'S, STS', and SGS'.

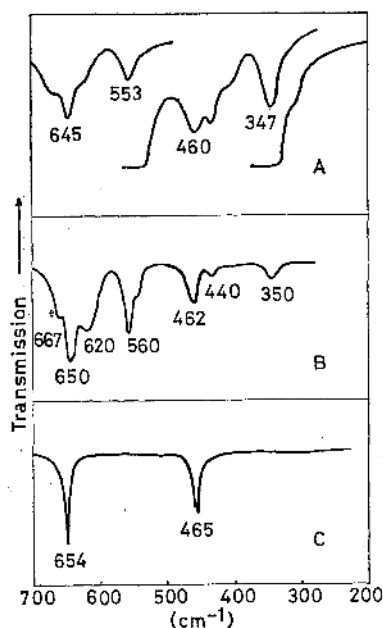
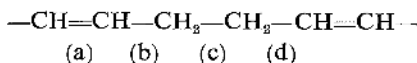


Figure 13. Infrared spectra of 1,5-hexadiene: (A) liquid; (B) glassy solid; (C) crystal.

As shown in Figure 13, the two CH_2 twisting bands near 650 and 560 cm^{-1} , which are ascribed to the *skew* and *cis* conformations of the $\text{CH}_2=\text{CH}-\text{CH}_2-$ group, consist of two or more bands in the liquid and amorphous solid states. This may be explained by the existence of many rotational isomers. The spectrum in the crystalline state has only one sharp CH_2 twisting band at 654 cm^{-1} , showing that one form, STS, SGS or STS', remains in the crystal. Among the above three forms only the STS' form has a center of symmetry. The fact that only two bands appear in this region in the crystalline state also covers the possibility of STS' being that form.

POSSIBLE CONFORMATIONS OF *trans*-1,4-POLYBUTADIENE

The possible stable conformations can be deduced from the information on the model compounds. The 1,4-polybutadiene chain has the following four axes in one unit:



For the *trans*-1,4-polybutadiene the axis (a) takes,

of course, *trans*, the axes (b) and (d) takes *cis* or *skew*, and the axis (c) takes *trans* or *gauche*. Study of the model compounds indicates that the *cis* form is almost as stable as the *skew* form in axes (b) and (d), although in the crystalline state all the molecules take the *skew* conformation. The energy difference between the *trans* and *gauche* forms in axis (c) is not certain. For the *n*-paraffin molecules and the polyethylene chain the *gauche* form is about 500 cal/mol less stable than the *trans* form. However, this is not always the case. For 1,4-polyisoprene the *trans* and *gauche* forms are equally stable.¹ This may be the case for 1,4-polybutadiene.

The crystal structure of *trans*-1,4-polybutadiene has been studied by Natta and Corradini¹⁷ and Iwayanagi, *et al.*¹⁸ It takes (TSTS') conformations for the (a), (b), (c), and (d) axes. This is one of the stable conformations discussed above.

The infrared spectra of *trans*-1,4-polybutadiene are shown in Figure 14. It has two peaks at 447 and 331 cm^{-1} at room temperature. When the film is heated at 70 – 80°C , the bands become

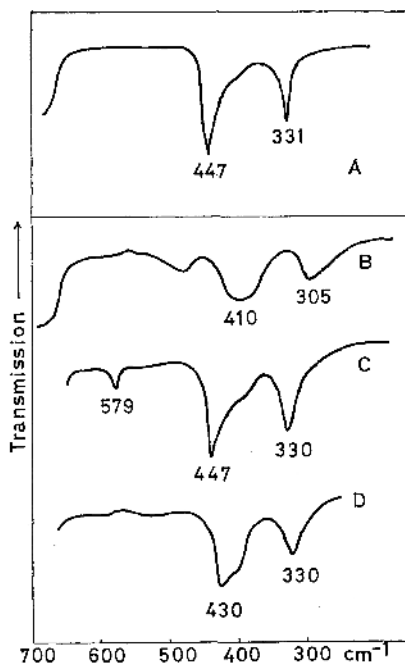


Figure 14. Infrared spectra of *trans*-1,4-polybutadiene: (A) film at room temperature; (B) film at 70 – 80°C ; (C) film cooled rapidly; (D) film annealed slowly.

broader and are shifted to the low frequency side. When the film is cooled rapidly, a weak band appear at 579 cm^{-1} in addition to the above two bands. When the film is annealed and cooled slowly the 579 cm^{-1} band does not appear.

It is of interest to compare these spectra with the spectra of *trans*-3-hexene given in Figure 11. The two peaks at 447 and 331 cm^{-1} of the polymer correspond to those at 483 and 323 cm^{-1} of *trans*-3-hexene, which belong to the STS' form. This correspondence coincides with the fact that the polymer chain takes (TSTS') conformation in the crystal.

That the two bands broaden and move to the low frequency side, when the film is heated, suggests that the polymer chain also takes the conformation (TCTS) or (TSTS), since the CTS and STS forms of *trans*-3-hexene have bands near 400 and 300 cm^{-1} , as shown in Figure 11. The CTS form has a band at 567 cm^{-1} . The fact that the polymer film which was cooled rapidly had a band at 579 cm^{-1} could indicate that the polymer chain partly assumes the (TCTS) conformation.

POSSIBLE CONFORMATIONS OF *cis*-1,4-POLYBUTADIENE

The number of possible stable conformations of the *cis* polymer is less than that of the *trans* polymer, since the axes (b) and (d) take only the *skew* conformation for the *cis* polymer chain. This is deduced from the stable conformations of *cis*-2-pentene and *cis*-2-hexene. The crystal structure of *cis*-1,4-polybutadiene has been studied by Natta and Corradini.¹⁹ The polymer chain takes the (CSTS) conformation.

The infrared spectra of the *cis* polymer are shown in Figure 15. All the observed bands at room temperature are very broad and are overlapped by each other, suggesting that the *cis* polymer chain takes many conformations consisting of CSTS, CSTS', and CSGS. The *cis* polymer shows a sharp and strong band near 590 cm^{-1} at low temperatures as shown in Figure 15. This may correspond to the 576 or 579 cm^{-1} band of *cis*-3-hexene given in Figure 10. The band corresponding to the 489 cm^{-1} band of *cis*-3-hexene is broad even at low temperature. This band is due to the torsion of the double bond

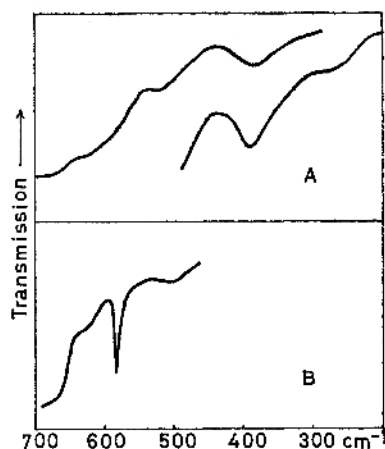


Figure 15. Infrared spectra of *cis*-1,4-polybutadiene: (A) film at room temperature; (B) film at low temperature.

which is inactive for *cis*-2-butene. The fact that this band is weak may provide information on the polymer symmetry.

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