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Molecular Vibrations and Structures of Polyalkyl Polysulfides. I. Polymethylene Disulfide

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The polarized infrared spectra of oriented sheets of polymethylene disulfide were measured in the 4000—200 cm^{-1} region, and the fiber period was found to be 4.18 Å by X-ray diffraction. It was found that this polymer does not have the expected twofold symmetry axes intersecting the helical axis at right angles. The infrared active normal vibrations of two likely structural models were calculated by the use of a modified Urey-Bradley force field. The structure of polymethylene disulfide was concluded to be the GG′G conformation along the sequence of the –S–CH$_2$–S–S– bonds of the 2$_1$ helical model.

Polyalkyl polysulfides $[(CH_2)_lS_m]_n$ are synthetic rubbers; one of them ($l=2$ and $m=4$) is commercially well known as Thiokol A. The present paper, the first of a series of reports on polyalkyl polysulfides, will deal with the molecular vibrations and the structure of polymethylene disulfide.

No studies have yet been reported on the molecular vibration and the structure of this substance. We therefore measured the polarized infrared spectra of an oriented sheet in the 4000—200 cm^{-1} region with a Perkin-Elmer 12C spectrometer. The fiber period of this substance was also measured by the X-ray diffraction method. The infrared active normal vibrations were calculated by the use of a modified Urey-Bradley force field, with the force constants transferred from the set obtained for simpler molecules with similar structures which we will report on separately.[1]

Experimental

The sample was prepared by the reaction of dichloromethylene and an aqueous solution of sodium disulfide, using magnesium hydroxide as an emulsifying agent. About three times as much sodium disulfide as was really needed was used in order to prepare high-molecular-weight samples. The reaction products were purified by continuous extraction with absolute alcohol, so that impurities and lower-molecular-weight polymers were washed out. Solid sheets were prepared by

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[1] M. Hayashi, Y. Shiro and H. Murata, to be published.

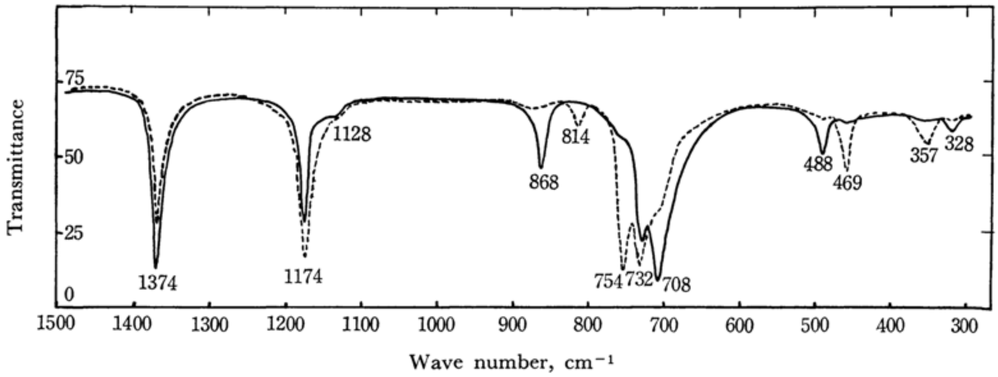

Fig. 1. Polarized infrared spectra of oriented film of polymethylene disulfide.
The solid curve was measured with the electric vector perpendicular and the broken curve with the electric vector parallel to the direction of orientation.

TABLE I. OBSERVED AND CALCULATED FREQUENCIES OF POLYMETHYLENE DISULFIDE (cm^{-1})

Observed[*1]	Calculated		Assignment[*4]
	GG'G[*2]	TGG[*3]	
	A species		
2980 m	2968	2969	CH$_2$ str.
2920 m	2896	2896	CH$_2$ sym. str.
1374 s	1369	1366	CH$_2$ scissor.
1174 s	1204	1210	CH$_2$ wag.
1128 sh	1118	1122	CH$_2$ twist.
814 w //	783	785	CH$_2$ rock.
754 s //	715	720	CS asym. str.
732 s	655	669	CS sym. str. (85), SCS def. (14)
469 m //	475	510	SS str. (90),
357 m //	358	338	SCS def. (46), CSS sym. def. (41)
	240	254	CSS asym. def. (45), SCS def. (32)
	166	177	CSS asym. def. (68). SCS def. (18)
	96	115	SS torsion (74), CS torsion (21)
	B species	E species[*5]	
2980 m	2968	2968	CH str.
2929 m	2896	2896	CH str.
1374 s	1368	1366	CH$_2$ scissor.
1174 s	1204	1209	CH$_2$ wag.
1128 sh	119	1121	CH$_2$ twist.
868 m ∠	781	787	CH$_2$ rock.
732 s	714	721	CS asym. str.
708 s ∠	664	673	CS sym. str. (84), SCS def. (15)
488 w ∠	487	514	SS str. (90)
328 w ∠	339	320	SCS def. (43), CSS asym. def. (38)
	259	245	CSS asym. def. (38), SCS def. (30)
	115	167	CSS sym. def. (78), SCS def. (18)
	49	111	CS torsion (64)
		13[*6]	

*1 The dichroism is shown as // and ∠ only for the infrared bands which exhibit clearly.

*2 The helical model is taken as 2_1.

*3 The helical model is taken as 4_1.

*4 Diagonal elements of potential energy distributions of the structural model GG'G are given in parentheses for mixed vibrations. (%)

*5 The phase differences are 180° for the B species of the GG'G form and 90° for the E species of the TGG form.

*6 The corresponding frequency is absent for GG'G since the phase difference is 180° for this case.

hot pressing, and then they were uniaxially oriented. The fiber period of the sample was determined to be 4.17 Å from the first and second horizontal layer lines on an X-ray rotation photograph. The orientation of the solid sheets was not, however, high enough for us to obtain more detailed information. The polarized infrared spectra were observed to be as shown in Fig. 1 and Table I.

Discussion

There are three internal rotation angles per chemical unit of polymethylene disulfide $[CH_2SS]_n$, one around the C–S bond and the other two around the C–S bonds. If we may assume that every chemical unit has the same structure, one set of these internal rotation angles is sufficient for specifying the structure of the entire helical polymer. Experimental data for simpler molecules, such as sulfur monochloride(2) and dimethyl disulfide(3), indicate that the only stable conformation for the S–S bond is the gauche form, with the internal rotation angle of 90°. On the other hand, for the C–S bonds, there are three stable forms, as evidenced by the experimental data for simpler molecules such as methyl ethyl sulfide.(4) These are the trans (the internal rotation angle of ca. 180°) and the two gauche conformations (ca. $\pm 60°$).

We will hereafter use symbols such as TGG for the models of the helical polymer, according to the system of notation used by Miyazawa et al.(5) For example, TGG implies that the internal rotation conformations along the series of $-S-CH_2-S-S-$ bonds are trans, gauche and gauche. The two gauche conformations which are obtained by clockwise and counterclockwise 60° rotations from the cis form are denoted as G and G′ respectively, while the rotation around the S–S bond is conventionally fixed as G (the internal rotation angle of 90°) throughout the treatment.

As Table II shows, there are six different possible helical conformations. In the same table are shown the expected fiber periods, the twofold symmetry properties, the number of repeating units, and the number of helical turns per fiber period. Two conformations, TTG and GGG, may be discarded, however, since the expected fiber periods are too much longer than the experimental value of 4.17 Å.

The fiber period of the TG′G conformation is calculated to be much longer than the measured value and to be a highly distorted structure. Therefore, this conformation may well be discarded also.

As for the molecular vibrations of this substance, it is expected that, in general, there are twenty-six or twenty-seven infrared active vibrations, which may be classified into two different groups (the groups belonging to the A and E species, or to the A and B species, respectively).(5)

There are fourteen pairs of degenerate vibrations belonging to the E species for the TGG structural model. For the G′G′G and GG′G models, there are thirteen non-degenerate B vibrations (with a phase difference of $\delta = 180°$) since these models are 2_1 helices. The bands due to these E or B vibrations exhibit a perpendicular dichroism.

On the other hand, the thirteen vibrations due to the A species exhibit parallel dichroism. However, if the conformation has twofold symmetry axes intersecting the helical axis at right angles, the vibrations belonging to the A species may be classified into two groups, A_1 and A_2, and the vibrations belonging to the A_1 species become infrared-inactive. There will then be seven A_1 and six A_2 vibrations.

As for the S–S stretching mode, there are, in general, one A vibration and one pair of E vibrations. If twofold symmetry axes exist, this A vibration belongs to the A_1 species and, hence, is infrared-inactive.

As is shown in Fig. 1 and Table I, however, we have observed two infrared bands around 470 cm^{-1} which can easily be assigned to the S–S stretching mode on the basis of the assignments given to simpler molecules, and also on the basis of the normal vibration calculations (to be described later). Since we expect no other vibration in this region, the above assignments of the observed infrared bands are reliable. The band at 488 cm^{-1} exhibits a perpendicular dichroism; it may be assigned to the E vibrations. On the other hand, the band at 469 cm^{-1} exhibits a parallel dichroism; it may be assigned to the A vibration.

As for the C–S stretching modes, we have two A vibrations and two pairs of E vibrations. If twofold symmetry axes exist, one of the two A vibrations belongs to the A_1 species and, hence, becomes infrared-inactive. In the expected region, we have observed three bands, at 754, 732 708 cm^{-1}. The band at 708 cm^{-1} clearly exhibits a perpendicular dichroism, but the band at 754 cm^{-1} clearly exhibits a parallel dichroism. Therefore, we may assign them to the E and A vibrations respectively. The band at 732 cm^{-1} also exhibits a parallel dichroism, but this band appears also to have a perpendicular component which shows up as a shoulder of the band at 708 cm^{-1} when the electric vector is perpendicular to the direction of orientation. Therefore, we may assign the band at 732 cm^{-1} to the A vibration, which is overlapped by the E vibrations. This assignment is also supported by the results of the normal vibration calculations.

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2) E. Hirota, This Bulletin, **31**, 130 (1958).

3) M. Hayashi, *J. Chem. Soc. Japan, Pure Chem. Sect. (Nippon Kagaku Zassi)*, **78**, 101 (1958).

4) M. Hayashi, T. Shimanouchi and S. Mizushima, *J. Chem. Phys.*, **26**, 608 (1957).

5) T. Miyazawa, ibid., **35**, 693 (1961); *J. Polymer Sci.*, **55**, 214 (1961).
T. Miyazawa, K. Fukushima and Y. Ideguchi, *J. Chem. Phys.*, **37**, 764 (1962), ibid., **38**, 2709 (1963).

TABLE II. STRUCTURAL MODELS OF POLYMETHYLENE DISULFIDE

Model	Internal rotation axes			Twofold symmetry axis*3	Expected fiber period	m_n*4
	S-C*1	C-S*1	S-S*1			
TTG	T	T	G	present	12 A	3_1
TGG	T	G	G	absent	4.18 A	4_1
TG′G	T	G′	G	absent	6.8 A	2_1
GGG	G	G	G	present	16 A	5_4
G′G′G	G′	G′	G	present	4 A	2_1
GG′G	G	G′	G	absent	4.18 A	2_1

*1 T, G and G′ denote the internal rotation angles of 180°, 60° and −60°, respectively.
*2 G denotes the internal rotation angles of 90°.
*3 Twofold symmetry axes intersecting the helical axis as right angles.
*4 *m*: the number of repeating units per fiber period.
n: the number of helical turns per fiber period.

TABLE III. THE FORCE CONSTANTS ($F'=-0.1F$)

(in md./Å)

K(CH)	4.28	H(CSS)	0.15	F(CSS)	0.25
K(CS)	1.69	H(SCS)	0.15	F(SCS)	0.5
K(SS)	2.37	H(HCS)	0.15	F(HCS)	0.39
p(CH)	−0.13	H(HCH)	0.32	F(HCH)	0.2
		(in md./Å)			
$\kappa(CH_2)$	0.0	$l(CH_2)$	−0.01	Y(CS)	0.054
Y(SS)	0.147	t	0.07	g	−0.05

p: CH bond streching interaction constant.
l: angle interaction constants between SCH.
Y: torsional constants.
t, *g*: trans and gauche angle interaction constants between SCH and CSS.

As for the SCS skeletal deformation mode, there is one A vibration, plus one pair of E vibrations. If twofold symmetry axes exist, this A vibration belongs to the A_1 species and, hence, becomes infrared-inactive. However, we have observed in the expected region the bands at 357 and 328 cm^{-1}, which exhibit a parallel and a perpendicular dichroism respectively.

The observation of the parallel bands due to the S–S stretching and SCS deformation vibrations indicates that the helical conformation of polymethylene disulfide does not have twofold symmetry axes intersecting the helical axis at right angles; we may therefore discard three structural models, TTG, GGG and G′G′G. Since TG′G has already been discarded, TGG and GG′G remain as the possible structural models for this substance. GG′G is a 2_1 helical model. Although TGG has two possibilities, 4_1 and 5_1, we think that the 4_1 helix is the most possible model because we have no example of 5_1 helices for other polymers. The values of the internal rotation angles were calculated so as to reproduce the measured fiber period. Two sets of values (195°, 70°, 90°, and 68°, −68°, 90°) were obtained for TGG and GG′G respectively on the assumption of the values of the bond lengths of r(C–S)=1.81 Å and r(S–S)=2.08 Å, and the valency angles of α(CSS)=105° and α(SCS)=109°28′.

We have also attempted to calculate the normal vibrations in order to confirm the assignments of the observed infrared bands, and also in order to examine whch structural model is more likely, TGG or GG′G.

For the calculation of the inverse kinetic energy matrix, values of r (C–H)=1.09 Å and α(HCH)=109°28′ were used besides the molecular parameters described for TGG and GG′G structural models. For the potencial energy matrix, a modified Urey-Bradley force field was used. This force field includes the same modifications as those used for simpler molecules such as dithiamethyl methane.[1] The modification terms are: (1) the torsional terms with the force constants Y; (2) the C–H bond interaction terms with the force constants p; (3) the angle interaction terms between the SCH angles with the force constants l, and (4) the angle interaction terms between the HCS and CSS angles with the force constants t and g. The last terms are the same type of correction terms as the trans and gauche interaction terms of the $-CH_2-CH_2-$ groups. For pairs of H and S atoms in the trans and gauche forms in the $-H_2CSS-$ group, the force constants t and g are used respectively. The force constants were all transferred from the set obtained for such simpler molecules as dimethyl disulfide and dithiamethyl methane.[1] They are listed in Table III. The method developed by

Miyazawa et al.[5] was used for the calculation. The results are shown in Table I.

First, it was found that the calculated frequencies agree satisfactorily with the observed frequencies in the higher frequency region. Second, significant differences are seen between the calculated low frequncies for the two possible structural models. For the S–S stretching vibrations, the calculated frequencies are 510 and 514 cm^{-1} for TGG, but they are 475 and 485 cm^{-1} for GG′G, while the observed frequencies are 469 and 488 cm^{-1}. The frequency agreements are much better for the GG′G model in their absolute values and also in the splitting of the A and E components. The same conclusion may be drawn from the analysis of one of the skeletal deformation modes and the C–S stretching modes. For other vibrations, such as the CH_2 deformation and C–H stretching modes, we did not find any essential differences between the different structual models.

Therefore, we may conclude that the polymethylene disulfide chain most probably has the 2_1 helical conformation of the GG′G type.

The assignments of the observed infrared bands are shown in Table I, together with the potential energy distributions.

For such other polymers as polyoxymethylene, the structural model, GG′G, has not been taken into consideration because of the intrachain steric impact.[6] It should be noted, however, that the situation is somewhat different for the polymethylene disulfide chain. The GG′G model is possible for this polymer because of the long bond lengths, r(S–S) and r(S–C), which tend to relax such steric impact.

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[6] T. Shimanouchi, *Kobunshi (High Polymers, Japan)*, **13**, 954 (1964).